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ABSTRACT

Analytical methods for determining important components of fission and natural radioactivity found in water are reported. The discussion of each method includes conditions for application of the method, a summary of the method, interferences, required apparatus, procedures, calculations and estimation of precision. Isotopes considered are cesium-137, strontium-90, lead-210, radium-226 and 228, tritium, and carbon-14. When two methods are in use for an isotope, both methods are reported. Techniques for the collection and preservation of water samples to be analyzed for radioactivity are also discussed. (CS)

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Techniques of Water-Resources Investigations of the United States Geological Survey

Chapter A5

METHODS FOR DETERMINATION OF RADIOACTIVE SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By L. L. Thatcher and V. J. Janzer, U.S. Geological Survey,
and K. W. Edwards, Colorado School of Mines

Book 5
LABORATORY ANALYSIS

SE 027 000

UNITED STATES DEPARTMENT OF THE INTERIOR

THOMAS S. KLEPPE, Secretary

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V. E. McKelvey, Director

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PREFACE

This series of manuals on techniques describes methods used by the Geological Survey for planning and executing water-resources investigations. The material is grouped under major subject headings called books and is further subdivided into sections and chapters. Book 5 is on laboratory analysis. Section A is on water. The unit of publication, the chapter, is limited to a narrow field of subject matter. "Methods for determination of radioactive substances in water and fluvial sediments" is the fifth chapter to be published under Section A of Book 5. The chapter number includes the letter of the section. The looseleaf format of this methods manual is designed to permit flexibility in revision and publication. Supplements, to be prepared as the need arises, will be issued to purchasers at no charge as they become available.

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METHODS FOR DETERMINATION OF RADIOACTIVE SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By L. L. Thatcher and V. J. Janzer, U.S. Geological Survey,
and K. W. Edwards, Colorado School of Mines

Abstract

Analytical methods for the determination of some of the more important components of fission or neutron activation product radioactivity and of natural radioactivity found in water are reported. The report for each analytical method includes conditions for application of the method, a summary of the method, interferences, required apparatus and reagents, analytical procedures, calculations, reporting of results, and estimation of precision. The fission product isotopes considered are cesium-137, strontium-90, and ruthenium-106. The natural radioelements and isotopes considered are uranium, lead-210, radium-226, radium-228, tritium, and carbon-14. A gross radioactivity survey method and a uranium isotope ratio method are given. When two analytical methods are in routine use for an individual isotope, both methods are reported with identification of the specific areas of application of each. Techniques for the collection and preservation of water samples to be analyzed for radioactivity are discussed.

Introduction

Purpose

This manual describes the analytical methods used by the U.S. Geological Survey for the collection and analysis of water samples for radioactive substances. The analytical methods are intended for the radiochemist who applies his expertise to the analysis of water. Adequate grounding in the principles and practice of radiochemistry is assumed. Therefore, such subjects as nuclear instrumentation, statistics, and radiation characteristics are not discussed. References are given to several excellent textbooks available on these subjects.

Generally, each analytical method is described in sufficient detail and is adequately referenced so that an experienced radiochemist could set up the analytical method with reasonable assurance of success. Two exceptions are: the determination of tritium by gas counting and the determination of carbon-14. Because of the complexity of the equipment and the extreme importance of certain critical details in both the instrumentation and operating procedure, any attempt to convey the fully detailed analytical procedure for direct duplication has a low probability for success. There is no substitute for actual operating experience in laboratories equipped for the gas-counting determination of tritium and the determination of carbon-14. For the above reasons, the descriptions of these two analytical procedures concentrate on the principles and major operating conditions involved.

In several analytical methods, reagents or equipment are cited by proprietary name. This is due to inadequate information on chemical composition on which to base a chemical name, or to special requirements known to be met by the cited reagent or equipment. In every case equivalent products that meet requirements may be substituted. No endorsement is intended.

Organization

Each determination includes a section on "Application," "Summary of the method," "Interferences," "Apparatus," "Reagents," "Procedure," "Calculations," "Report" (of results), and "Precision." The "Calculation" section under each determination differs slightly from the practice in chapter A1 in that reference is made to a general equation

when possible. Radioactivity calculations for different nuclides follow similar principles which can be summarized in a general equation. The general equation, with its modifications to fit particular requirements, is considered in a following section.

Nuclear data

Data on half-lives were taken from the "Chart of the Nuclides" (Holden and Walker, 1969). Data on decay schemes and energies of nuclear radiation were taken from "Table of Isotopes" (Lederer and others, 1968). The "Chart of the Nuclides" was reproduced in "Radiological Health Handbook" (U.S. Dept. of Health, Education, and Welfare, 1970), and data on the more important nuclides listed in Lederer, Hollander, and Perlman (1968) were also reproduced in the HEW publication.

Unit, symbols, and abbreviations

Terms that are generally used throughout the text are listed below. Terms that are used infrequently, usually in connection with one analytical method, are defined at the first usage in the text. Terms that are used in calculation of data are defined under the general equation in the "Calculations" sections.

Ci ——curie (3.7×10^{10} disintegrations per second)
μCi ——microcurie (3.7×10^{4} disintegrations per second)
pCi ——picocurie (3.7×10^{-2} disintegrations per second)
μCi/l —microcuries per liter
pCi/l —picocuries per liter

cpm —counts per minute
dpm —disintegrations per minute

keV —thousand electron volts
MeV —million electron volts

d ——day
hr ——hour
min —minute
sec ——second
yr ——year

e ——2.718....., base of the natural logarithms
ln ——logarithm of any number N, to the base e
log ——logarithm of any number N, to the base 10

ml ——milliliter
gal ——gallon (3.785 liters)

m ——meter
cm ——centimeter
mm —millimeter
in. ——inch (2.54 cm)
ft ——foot (30.48 cm)

g ——gram
mg ——milligram

M ——molarity of a solution
N ——normality of a solution
meq —milliequivalent
psi ——pounds per square inch

Sources of radioactivity in water

Radioactivity in water may be of natural or artificial origin. The principal natural processes that bring radioactivity into water are the weathering of rocks containing radioactive minerals and fallout of cosmic-ray-produced nuclides. The major sources of artificial radioactivity are the nuclear power industry, nuclear weapons testing, and the peaceful applications of nuclear materials and devices.

Natural radioactivity

The principal radionuclides introduced naturally into surface and ground waters are uranium, radium-226, radium-228, radon, potassium-40, tritium, and carbon-14. All but the last two derive from radioactive minerals. Radioactive elements including uranium, thorium, and actinium and radioactive daughters resulting from these decay series are important primarily for reasons of health and as potential energy sources. These three natural decay series are headed respectively by uranium-238 (half-life 4.51×10^{9} yr), thorium-232 (half-life 1.41×10^{10} yr), and uranium-235 (half-life 7.13×10^{8} yr). In areas of the world where radioactive minerals are particularly abundant as in the Joachimsthal region of Czechoslovakia, the Minas Gerais region of Brazil, and the Colorado Plateau of the United States, radioactivity in some waters may greatly exceed the average concentrations

present in most continental waters. Dissolved natural uranium is the major radioactive constituent in most of these waters.

Tritium and carbon-14 are produced by the interaction of cosmic-ray neutrons with nitrogen in the upper atmosphere. The tritium is eventually rained out as tritiated water, and the radiocarbon is incorporated into atmospheric carbon dioxide. The principal reservoir for both radionuclides is ultimately the ocean. Both radionuclides are also produced by thermonuclear weapons testing. In 1963, the year when radioactive fallout reached its maximum, the atmospheric concentration of thermonuclear tritium exceeded that of natural tritium by approximately 3 orders of magnitude. The additional carbon-14 of thermonuclear origin was much lower and approximately equalled the carbon-14 naturally in the atmosphere. Radioisotope concentrations in fallout have diminished rapidly since 1963 as a source of radioisotopes in water. Tritium is also a fission product, and by 1970 the nuclear power industry had probably become the largest source of tritium (Jacobs, 1968).

Artificial radioactivity

Nuclear waste disposal is the principal possible source for the leakage of artificial radionuclides (fission products and activation products) into water. Most of the waste is derived from the reprocessing of nuclear fuel. Reprocessing is required at intervals to remove neutron-absorbing fission products and to recover the uranium and plutonium. Until reprocessing, 99.9 percent of the fission and activation products produced remain locked inside the fuel element. The fuel element is dissolved in acid, and chemical separations of the highly radioactive wastes are carried out. The final waste consists of a low-level solution, which may be sent to seepage ponds, and a high-level solution or "hot" solution that must be stored for many years to allow radioactive decay. Strontium-90 (half-life 28.9 yr), cesium-137 (half-life 30.2 yr), iodine-129 (half-life 1.6×10^{7} yr) and plutonium-239 (half-life 24,390 yr) are major radioisotopes of concern. It is estimated that by 1980, several million gallons of high-level waste with radioactivity on the order of 10 billion curies will be in storage as a result of nuclear power production (Hogerton, 1963, p. 448).

A relatively smaller amount of radioactivity may leak to the environment as a result of daily operation of a nuclear powerplant because of neutron activation of salts in the coolant water, neutron activation of dissolved corrosion products, and possible release of fission products by a defective fuel element. Although every nuclear powerplant has built-in safeguards against release of radioactivity, the possibility of accidental leakage must always be considered.

In addition to tritium and carbon-14, aboveground nuclear weapons testing releases strontium-90, radiocesium isotopes, iodine-131, and other nuclides to the environment. The fraction of these radionuclides that fall out or rain out into water bodies or watersheds constitute a significant source of water contamination.

Peaceful applications of nuclear explosives, such as nuclear gas stimulation and nuclear mining, present a possible source of locally intense contamination of ground water. If venting occurs, the possibility of contamination of surface water by fallout also exists.

Nuclear research laboratories, hospitals, and the very limited number of industries that use radioactivity constitute a relatively minor source of possible radionuclide leakage, but may be of local significance.

Measureable radioactive material may derive from sources not normally considered radioactive. Examples are fly ash from the combustion of fossil fuel (coal may contain uranium and radium) and the ceramics industry (uranium salts are used in the preparation of some glazes).

Permissible concentrations of radioactivity in effluents to unrestricted areas

Current values are tabulated in Part 20, "Standards for Protection Against Radia-

tion," published and updated periodically by the U.S. Nuclear Regulatory Commission (1976). The Commission is the source of the permissible concentrations of radioactivity in effluent (PCRE) values reported for the nuclides in this manual. The significance of the values and the basis for their computation is described in National Bureau of Standards (NBS) Handbook 52 (1953) and NBS Handbook 69 (1959). The U.S. Public Health Service has published recommended maximum concentrations for radium-226, strontium-90, and gross beta activity in drinking water (Drinking Water Standards, 1962). Updated standards published in "Water Quality Criteria, 1972" (1973) are quoted in addition, when applicable.

Additional drinking-water regulations were published in the Federal Register, volume 41, No. 133, July 9, 1976, as a supplement to Title 40, Code of Federal Regulations (CFR), Part 141. The National Interim Primary Drinking Water Regulations (Part 141) have been published (1975), but were in the process of revision at the time this paper was written.

Radiological safety

The radiochemist or chemist who uses the methods in this manual should have an adequate training in radiological health and safety practice in the laboratory. Such training is a requirement for obtaining the U.S. Nuclear Regulatory Commission license to use radionuclides. Analysis of even environmental-level samples will generally require the use of various radioactive calibration planchets or standardized solutions, some of which are hazardous if not properly used. Discussions of various aspects of radiological safety are given in the following suggested references. An introduction to the subject is found in the chapter on the radiological laboratory in "Guide for Safety in the Chemical Laboratory" (M.C.A., 1954). A comprehensive exposition of radiological health physics is found in "Principles of Radiation Protection" (Morgan and Turner, 1971). The safety series of the International Atomic Energy Agency includes reports of particular value to laboratory users of radioactivity. "Safe Handling of Radioisotopes" (1962) and the "Health Physics Addendum" (1960) are cited. Precautions against contamination and procedures for decontamination are detailed in the National Bureau of Standards publication "Control and Removal of Radioactive Contamination in Laboratories" (1951). Procedures to be followed in event of an accident involving radioactivity are described in "Medical Aspects of Radiation accidents" (Saenger, 1963).

Geochemistry of radioactivity in water

Dissolved and particulate radioactivity in water is controlled by the same mechanisms that affect other trace and macro constituents in the geohydrologic environment. Radioactive disintegration of an atom by alpha and beta decay results in the formation of an atom of a new element, frequently in an excited state. Gamma emission results from such an atom in the excited state going to a lower energy state. The geochemical behavior of a daughter element may be grossly different from that of the radioactive parent, although its occurrence, distribution, and transport may be governed by the parent.

Carbon-14

Carbon-14 is the radioactive isotope of carbon with a half-life of 5,730 years. The older half-life value of 5,568 yr is generally used for the calculation of ages in order to maintain consistency with carbon-14 dates in the older literature. Ages based on the older half-life value are converted to the basis of the newer half-life by multiplying by 1.03. Carbon-14 decays by the emission of a beta particle with the low maximum energy of 156 keV.

Neutrons produced by primary cosmic radiation interact with stratospheric nitrogen to produce carbon-14 and hydrogen:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H.$$

The rate of production in the atmosphere is estimated at approximately 2.4 atoms per second per square centimeter of the Earth's surface (Libby, 1955). Carbon-14 is also a product of thermonuclear weapons testing. This source had approximately doubled the atmospheric concentration of carbon-14 and had increased the concentration in surface ocean water by about 20 percent by the late 1960's (Nydal, 1966). Possible contamination of ground waters by thermonuclear carbon-14 imposes a severe limitation to the application of carbon-14 dating.

Carbon-14 produced by cosmic radiation is oxidized to carbon dioxide and is transported to the lower atmosphere by mixing processes where it enters the biological cycle. Some radioactive carbonates enter the hydrological cycle and provide the basis for carbon-14 dating of older ground waters. The specific activity of cosmic-ray produced carbon-14 in the atmosphere, surface waters, and all living matter was determined by Libby (1955) to be 16 dpm per gram of carbon, but is now considered to be lower. Suess (1965) determined 14 dpm per gram of carbon.

The specific activity of carbon-14 in carbonaceous material cut off from contact with the atmosphere, such as the carbonate species in ground water, decreases at a rate controlled by the carbon-14 half-life. The carbon-14 to carbon-12 ratio is also affected by exchange of carbonates between the water and aquifer, biochemical effects, and possible reactions with silicates. Compensation for exchange effects has been attempted through the carbon-13 to carbon-12 ratio (Pearson, 1965).

Cesium-137 and cesium-134

Eleven cesium isotopes are fission products, but usually only cesium-137 is significant to water quality. Cesium-134 is produced in fission by the neutron activation of cesium-133, a fission product. The half-life of cesium-137 is 30 yr and that of cesium-134 is 2.7 yr. Cesium-137 has been deposited throughout the world, with much higher concentrations in the Northern Hemisphere than in the Southern Hemisphere as a result of nuclear weapons testing.

Either the beta or gamma radiation associated with the cesium isotopes may be used for their detection. Detection by beta radiation is more sensitive but less specific. The use of gamma radiation permits distinguishing between the isotopes by means of energy discrimination since the energy peak for cesium-137 (barium-137m) is at 662 keV, and the principal peaks for cesium-134 are at 605 keV and 796 keV. Preconcentration of the radiocesium is used before counting, in either case, to permit detection at low environmental levels. Four to 20 liters of sample have been used with the gamma-counting technique depending on sensitivity required. A few hundred milliliters are usually adequate for the beta-counting technique.

Lead-210

Lead-210 originates from the decay of radon-222. The isotope is a beta emitter with half-life of 22 years. Lead 210 formed underground is probably trapped on exchange sites of clay minerals or other reactive material and presumably has very limited migration. The lead-210 formed by decay of atmospheric radon enters the hydrologic cycle principally through precipitation. A smaller part is removed from the atmosphere as dry fallout. Most of the lead-210 falls on the oceans where it finds use as a tracer for the investigation of vertical mixing. Some lead-210 enters terrestrial surface waters and the permanent snow fields. The half-life is convenient for dating more recent snow deposits, and the natural level of lead-210 has not been upset by nuclear weapons testing as is the case with tritium. Estimation of the lead-210 input through precipitation, a requirement for dating of snow and ice, must be based on actual measurements of the lead isotope since calculation on the basis of equilibrium with prevailing radon concentrations is not accurate. This was shown by Patterson and Lockhart (1964) who made a latitudinal survey of lead-210 in ground-level air.

The lead-210 content of precipitation appears to vary greatly with individual storms, probably depending on the trajectory of the air mass. Rama and Goldberg (1961) reported 0.05 pCi/l for surface ocean water and 0.13 to 6.7 pCi/l for Colorado River water. Holtzmann (1964), using the more sensitive polonium-210 alpha-counting technique, found an average of 0.127 pCi/l of lead-210 in untreated Illinois surface waters and 0.051 pCi/l in well waters. As expected, the sorption of lead by soil reduces the concentration in ground water. Holtzmann found that lead-210 concentrations in potable waters of Illinois were generally much below radium-226 concentrations.

Radium

Radium is a radioactive member of the alkaline-earth family that is widely disseminated throughout the crust of the Earth. Four isotopes of radium are members of the three natural radioactive series. The isotopes with their natural series and decay data are listed below.

Isotope	Series	Half-life	Decay mode
Radium-223	Actinium	11.43 d	α
Radium-224	Thorium	3.64 d	α
Radium-226	Uranium	1,602 yr	α
Radium-228	Thorium	5.75 yr	β

The concentrations of the radium isotopes in geologic and hydrologic materials vary greatly in nature depending on the uranium and thorium concentrations in the source and the geochemical history of the material.

Chemically, radium is analogous to barium; the carbonates, sulfates, and chromates are insoluble, while the chlorides, nitrates, and hydroxides are soluble in water. The distribution of radium is governed more by the distribution of uranium and thorium, however, than by the geochemistry of radium.

Radium-226 and radium-228 are the most important isotopes of radium found in water because of their longer half-lives, health significance, and as geochemical indicators of uranium and thorium respectively. On the basis that the world abundance of thorium is approximately three times that of uranium and the specific activity of thorium-232 is approximately one-third that of uranium-238, the world activity inventories of radium-226 and radium-228 should be roughly equal. World activity inventory for radium-224 should also be equal to that of radium-228 since the two are in radioactive equilibrium. The local relative abundances of the 226 and 228 radium isotopes may vary greatly, however, as a function of the local uranium to thorium ratios. Also there may be extreme local variations in the ratio of radium-228 to radium-224 because the latter is produced from the former through an actinium and a thorium isotope. Because the geochemistry of actinium and thorium are significantly different from that of radium, there is great opportunity for local disequilibria.

Radium is found in waters from most geologic terranes because of the wide distribution of the parent elements in nature. Concentrations of radium-226 in freshwater usually are less than 1–2 pCi/l. Concentrations of radium-226 in the Cambrian and Ordovician limestones of North Central United States often exceed 3 pCi/l, and in certain aquifers of the Colorado Plateau, the concentration may be much higher (Scott and Barker, 1959). Water that leaches waste piles from uranium mining and milling operations may contain radium at much higher levels.

While most of the radium investigations have centered on the 226 isotope, work in the U.S. Geological Survey has shown the importance of radium-228. Johnson (1971) reported that concentration of radium-228 in several streams of the Front Range near Denver exceeded the concentration of radium-226. This agrees with the twice normal abundance ratio of thorium to uranium for the area. Krause (1959) reported relatively high concentrations of radium-228 in wells tapping deep ground-water aquifers in Iowa, Wisconsin, Illinois, and Missouri.

All radium isotopes are hazardous because of the bone-seeking properties of the element. Concentrations in the bone can lead to malignancies. The U.S. Public Health Service has recommended 3 pCi/l as the upper limit

for radium-226 in water for public consumption. The U.S. Nuclear Regulatory Commission (NRC) (1976) gave the following permissible concentrations of radioactivity in effluent (PCRE) values for radium (soluble) in waste solutions that may be released to water bodies accessible by the public:

Radium-223	700 pCi/l
Radium-224	2,000 pCi/l
Radium-226	30 pCi/l
Radium-228	30 pCi/l

The "Water Quality Criteria, 1972" (EPA, 1973) recommended a radium-226 intake limit of 0.5 pCi/d. Assuming a 2 l/d consumption rate, this is equivalent to a 0.25 pCi/l concentration limit.

Three analytical methods for radium isotopes are reported, each serving a different purpose. A determination of the gross alpha radioactivity of radium is the simplest procedure and is satisfactory where identification of individual alpha-emitting isotopes is not required. A second procedure is specific for radium-226 and a third for radium-228.

Ruthenium-106 and ruthenium-103

Ruthenium-106 and ruthenium-103 are the important ruthenium isotopes produced in nuclear fission. They may be present in precipitation and surface waters after atmospheric nuclear testing. The short half-life of ruthenium-103 (39.3 d) essentially rules out its presence in ground water. Ruthenium-106 (half-life 368 d) may be found in ground water in the immediate vicinity of underground nuclear tests. Both isotopes are beta emitters with maximum energy of 0.0392 MeV for ruthenium-106 and maximum energy of 0.70 MeV (3 percent) and 0.22 MeV (97 percent) for ruthenium-103. Ruthenium-106 is determined by counting the daughter, rhodium-106, with which it is in secular equilibrium. The more energetic beta particles of rhodium-106 (3.53, 3.1, 2.4, and 2.0 MeV,) are more easily detected.

The NRC–PCRE value for ruthenium-106 in effluents released to uncontrolled areas is 1×10^{-5} μCi/ml (10,000 pCi/l). Ruthenium concentrations determined by procedure R–1150–76 are reported as ruthenium-106, although ruthenium-103 may also be present in the sample. After 8 months decay (6 half-lives), the ruthenium-103 concentration is usually insignificant.

Strontium-90

Nuclear fission produces two important isotopes of strontium: strontium-90 (half-life 38.9 yr) and strontium-89 (half-life 50.8 d). Although the latter nuclide has initially greater activity, the longer half-life of strontium-90 makes it more significant to worldwide environmental pollution. Except for short periods following atmospheric nuclear testing, strontium-90 is the predominant radioisotope of this element on the Earth's surface. This nuclide is now widely distributed in man's environment from stratospheric and tropospheric fallout. Higher concentrations exist in the Northern Hemisphere. It is often detected in soils, foods, water, and biological materials. The "Water Quality Criteria, 1972" (EPA, 1973) recommended limit on strontium-90 intake in water used for public supply is 5 pCi/d. Assuming a 2 l/d consumption rate, this is equivalent to a 2.5 pCi/l concentration limit.

Tritium (hydrogen-3)

Tritium is the radioisotope of hydrogen with atomic weight of 3. It decays by pure beta emission with half-life of 12.33 yr. The beta particles have an average energy of 5.7 keV and maximum energy of 18.6 keV. Tritium is formed in the upper atmosphere by cosmic-ray spallation and by the interaction of fast neutrons with nitrogen:

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{3}_{1}\mathrm{H} + {}^{12}_{6}\mathrm{C}.$$

The natural production rate of tritium is on the order of 30 atoms per square centimeter of the Earth's surface per minute. (Kaufman and Libby, 1954).

Tritium is also produced by thermonuclear weapons testing. The first tritium from this source was detected in 1952, and by 1954 the thermonuclear tritium was substantially greater than the natural tritium. (Begemann

and Libby, 1957). Thermonuclear tritium reached a peak in 1963 when the concentration in the Northern Hemisphere exceeded the natural level by approximately 3 orders of magnitude.

Tritium is principally of interest to the hydrologist as a water-dating tool and as a tracer, introduced either naturally or artificially, for investigating ground-water hydrodynamics in areas of relatively rapid flow. The tritium dating of ground water that entered as recharge before 1952 is based on radioactive decay of tritium and the "prebomb" concentration of approximately 8 tritium units (Tu), (1 Tu=1 T atom/10^{18} H atoms) determined by Kaufmann and Libby (1954).

The dating of ground water originating as recharge after 1954 is based on the correlation of tritium concentrations in the ground water with known fallout peaks. The applications of tritium in hydrology are reviewed by Thatcher (1969).

Tritium is also of interest in public health inasmuch as concentrations much exceeding the natural level may be released to the environment in the course of tritium tracer experiments, nuclear power production, weapons testing, nuclear waste disposal, and "Plowshare" activities. "Water Quality Criteria, 1972" (EPA, 1973) notes that a tentative limit of 3,000 pCi/l of tritium has been prepared for the revised edition of "Drinking Water Standards." The NRC (1975) PCRE value for tritium in effluents released to uncontrolled areas is 3 μCi/l. The liquid-scintillation counting technique provides all the sensitivity required for monitoring tritium concentrations at the levels significant to public health.

Although tritium is not a major fission product, there is a significant production of tritium in nuclear power reactors. The greater part of the tritium remains enclosed in the fuel element until the latter is dissolved for reprocessing. The production of tritium in reactors depends greatly on the reactor type, and estimates of total production are subject to many uncertainties. It seems clear, however, that the reactor contribution to the tritium inventory is substantial. Sources of tritium have been reviewed by Jacobs (1968).

Determination of tritium radioactivity is complicated by the very low energy of the beta radiation which necessitates mixing the tritium intimately with the counting medium. Gas phase counting is carried out by introducing the tritium as a gas (HT) into a proportional counter containing the proper pressure of hydrocarbon gas to assure operation in the proportional region. Liquid scintillation counting of tritium is carried out by mixing the tritiated water sample with an organic scintillator suspended or dissolved in an organic medium compatible with water. The efficiency of gas phase counting may be very high, 60–80 percent. The efficiency of liquid scintillation counting is on the order of 20–25 percent.

Since the decay rate for 1 Tu concentration in water is only 0.007 dpm/ml and the background count (gas counting) is on the order of 2 cpm, it is obvious that enrichment of the tritium in the water sample is required when low concentrations of tritium are to be determined. Enrichment is carried out by electrolysis using essentially the same process as is used for the preparation of heavy water. Passage of electric current through water results in the liberation of the light hydrogen isotope (protium) at a faster rate than the heavy isotopes (deuterium, tritium), thus enriching the latter in the residual water.

Uranium

Uranium is widely disseminated in the lithosphere, and most natural waters contain detectable concentrations of this element. The average concentration in the ocean is about 3 μg/l (Rona and others, 1956). The uranium content of ground and surface waters varies greatly, from less than 0.1 μg/l to several milligrams per liter (mg/l). In most natural waters the concentration is less than 10 μg/l. The limit on uranyl ion (UO_2^{+2}) in public supplies (Water Quality Criteria, 1972) is 5 mg/l.

Dissolved uranium in natural waters exists principally as uranyl ion (UO_2^{+2}) which may

be complexed with carbonate. While uranium in surface waters is almost entirely hexavalent, there may be an appreciable percentage of tetravalent uranium under reducing conditions found in some ground waters. The latter is predominantly complexed and is highly insoluble in basic solution.

Uranium in natural water is important in geochemical prospecting and as an indicator of pollution from mining operations. It is unlikely that uranium could reach concentrations significant to health, although a high concentration of uranium could be indicative of possible high levels of the much more hazardous radium isotopes.

There are the three natural uranium isotopes:

Isotope	Abundance (percent)	Half-life (yr)
U-238 (U series)	99.27	4.51×10^{9}
U-235 (Ac series)	.72	7.1×10^{8}
U-234 (U series)	.006	2.47×10^{5}

Uranium-234 is related to uranium-238, the parent of the uranium decay series, by the following decay sequence:

$$U^{238} \xrightarrow{\alpha} Th^{234}\,(24.1\text{ d}) \xrightarrow{\beta} Pa^{234}\,(1.18\text{ min}) \xrightarrow{\beta} U^{234}.$$

The total world radioactivities of the 234 and 238 isotopes must be equal since the two are in secular equilibrium. Local physical and chemical effects may result in local disequilibria which are of geochemical interest and have been given intensive study. Disequilibria may result from physical or chemical mechanisms. The principal physical mechanism is the energetic alpha recoil associated with the decay of uranium-238 to thorium-234. This may rupture chemical bonds and permit thorium to go into solution in ground water where it decays to uranium-234. Although thorium is considered to be sorbed by sediment, the presence of dissolved organic matter or other complexing agents may tend to stabilize it. Since both intermediates, thorium-234 and protoactinium-234, are chemically different from uranium, chemical differentiation may occur. Difference in oxidation state between the 234 and 238 isotopes can have an additional effect. These effects frequently lead to enrichment of uranium-234 in water (Chalov and others, 1964; Cherdyntsev and others, 1961; Thurber 1962). Depletion of the 234 isotope is less common. Isotopic dating of waters, correlation of disequilibria with rapid leaching (important in pollution studies), and the geochemistry of uranium transport are examples of the possible application of uranium isotope disequilibria studies.

While the usual objective of the analysis is determination of the uranium-234 to 238 activity ratio, it is also possible to determine the activity ratio of the 235 isotope to 238. The uranium-235 to 238 ratio is constant (1:137) in the absence of artificial depletion or enrichment. Therefore, an increase of the 235 isotope is reason to suspect the presence of material processed for nuclear fuel.

Collection and treatment of samples

The principal requirements to be met in sampling a water body for the determination of radioactive constituents are the same as for other constituents, that is, collection of samples in an orderly sequence that provide a representative analysis of the water body both areally and temporally. Considerations involved in setting up a sampling program that yields the required representative information are discussed in detail in an earlier chapter (Brown and others, 1970) in this series of Techniques of Water Resources Investigations of the U.S. Geological Survey. Reference is made to the earlier chapter for discussion of site selection, sampling frequency, equipment, sample identification, and other elements of an organized sample-collection program. Guidelines for the collection and field analysis of ground-water samples are given by Wood (1976). If analyses for the determinations described in this manual are to be made by a U.S. Geological Survey Water Resources Division central laboratory, the appropriate section chief should be contacted. Specific information can then be obtained for collecting the samples, obtaining the necessary sampling supplies, and so forth.

The overriding problem in sampling for radioactivity is preservation of the extremely dilute concentration of radionuclides (usually in the nanogram- and picogram-per-liter range) in their original conditions until the analysis can be performed. While preservation of the original condition of the sample is a general problem in water analysis, the extreme dilution of the radionuclides greatly intensifies the problem. Although extensive research has been given to the chemistry of extremely dilute solutions, the practical results in terms of preservation of the sample have not been completely effective. Indeed, conclusions from different investigations are often at variance, and indicate that the essential phenomena are not completely understood.

Early in the history of radiochemistry the term "radiocolloid" came into use as a result of apparently colloidal phenomena observed in radioisotope solutions (dialytic separation, nonionic migration behavior in the electric field, and so forth). Although radioactivity produces electrically charged centers (which could attract other ions to form aggregations), it is unlikely that the phenomena in very dilute solutions of radioisotopes are greatly different from phenomena in very dilute solutions of nonradioactive ions. Starik (1959) has exhaustively reviewed the earlier work and finds both colloidal and noncolloidal behavior depending on conditions.

Starik also investigated the effect of filtration and found that radioisotopes were retained in varying ratios by different filter media depending upon the pH and other chemical factors. Overall, both sorption loss and filtration loss are functions of the concentration, pH, oxidation state, electrolyte composition, and presence of traces of colloidal material in the solution such as colloidal silica as well as numerous other factors. Many observations of "radiocolloids" are apparently attributable to sorption of the radionuclide on traces of colloidal silica.

Tests suggest that the sorption loss in natural-water samples, as against sorption loss in very dilute distilled-water solutions, may be relatively small. Many of the tests reported in the literature are based on distilled-water solution, and thus are not entirely relevant.

Similar tests with uranium showed no significant loss under any condition. Hexavalent uranium is stable in natural water exposed to the atmosphere, particularly when bicarbonate is present. Earlier tests by Janzer (unpub. data) are in agreement with the above findings. Surface-water samples were collected in polyethylene bottles under three conditions: no treatment, filtered and acidified at time of collection, and filtered at time of collection but not acidified. The concentrations of radium, uranium, and gross alpha-beta activity determined repetitively in all three samples agreed closely and did not significantly change with time.

It is generally recommended that acid should be added to very dilute solutions of trace elements for the purpose of minimizing sorption loss of trace elements from the solution while it is in contact with a sample container. This is the practice recommended herein, but it should be noted that the experimental evidence is not at all conclusive. There appears to be significant evidence from both radioactive and nonradioactive work with trace elements that the individual chemistry of the elements must be considered, and optimum preservation techniques for each element, or for chemically related groups of elements, are required. Starik (1959) reported, for example, that polonium is sorbed most strongly (on glass) at pH 4.5, and while the sorption is much less below pH 4, it is reduced to the minimum above pH 8. He also reported minimum sorption of radiotantalum at pH 10 with maximum sorption at pH 3.5, and maximum sorption of niobium-95 at pH 2.

Ground-water samples are usually clear initially but may become turbid as hydrated iron and manganese oxides form on exposure to air. It is essential to prevent the formation of these precipitates because they can coprecipitate radioactive elements. Precipitation of hydrous oxides is prevented by acidifying the sample after filtration. Sufficient reagent grade hydrochloric or nitric acid should be

added to the filtered sample to obtain a pH of 1 or less.

A 4-liter sample is usually adequate for radiochemical analysis of gross alpha, gross beta, uranium, and radium. Additional sample may be required if other analyses or reruns are desired. Recommended sampling procedures for surface and ground waters are described as follows:

1. Collect and store the samples only in specially washed and labeled 4-liter polyethylene sampling bottles provided by the radiochemical laboratory. The bottles are cleaned by the following procedure: Wash with tap water; add 10 ml nitric acid, and refill with tap water; allow to stand overnight; empty, and finally rinse several times with small amounts of distilled water; and drain, and allow to dry before capping and storing.
2. Surface-water samples are collected to obtain a representative sample of well-mixed water at a single point, generally near the center of the stream or river if possible. Preferably only clay- or silt-sized particles should be present in the sample if samples are to be analyzed for suspended gross alpha and beta radioactivity. No filtration or acidification is usually required if dissolved and suspended gross alpha and beta radioactivity and dissolved radium or uranium are desired. (Other analyses may require special handling, and the appropriate Central Laboratory section chief should be contacted for specific details.) Leave an air space of several centimeters to allow for volume changes with temperature. Seal the cap with vinyl tape. Ground-water samples should be filtered through a 0.45-micrometer membrane filter at the time of collection. Add sufficient reagent-grade hydrochloric acid (preferred), or nitric acid, to lower the pH to approximately 1. Minimum value of concentrated acid that should be added to a 4-liter sample is 8 ml. Alkaline waters may require more acid. Test with pH paper. Seal the cap with vinyl tape.
3. At the time of collection, fill out appropriate sample data form as completely as possible and include with the sample in the manner prescribed by the analyzing laboratory. When compiling the results of the analysis, it is essential to have all the information possible pertaining to the conditions which existed at the time the sample was collected.
4. Box the samples in the cartons provided, and ship as soon as possible after collection. Be sure that return address is on the shipping label.
5. During winter months, it is essential to mark the cartons "Water Sample. Keep from freezing."

When sampling a ground-water system for tritium or carbon-14, it is particularly important to select the sampling wells with care so that a representative sample is obtained. The well should be properly sealed to minimize surface-water contamination, and it should preferably be in constant use. A highly productive well is preferred to a low-yield well. The well should be thoroughly pumped before the sample is taken. A perfectly dry bottle or barrel is used. During and after the collection of the sample, minimize contact with the atmosphere which may contain carbon-14 and tritium at concentrations ranging from several-fold to several orders of magnitude higher than the radionuclide in the water sample.

Calculations of radionuclide concentrations

The method used to calculate concentrations of radionuclides for most of the determinations in this manual may be expressed in the form of a general equation. Exceptions are the calculations for uranium, uranium isotope ratio, and carbon-14 age. The general method of calculation compares the activity of a sample against the activity of a standard, and corrects for decay of the radionuclide in the sample between time of collection

and time of analysis. If the recommended practice of minimizing time delay between sampling and analysis is followed, the correction for decay through this interval becomes negligible for many radionuclides.

A more significant correction is that necessitated by decay of the standard between the date of its certification by the National Bureau of Standards (or other supplier) and the date of its use to calibrate the analytical method. This time interval may amount to several years and is significant, relative to the half-lives of several radionuclides.

The following general equation applies when in-growth of daughter activity is not a factor, and when the half-life is long relative to the counting time. This is the usual situation.

$$C = \frac{1000\bar{c}}{KVEf(e^{-\lambda t})}, \qquad (1)$$

where

C = concentration of radionuclide. This is usually expressed in pCi/l.

$\bar{c} = \bar{c}_s - (\bar{b}_1 + \bar{b}_2)$. Average count rate of the sample in counts per minute (cpm) after correction for background and blank,

where

$\bar{c}_s$ = average gross sample count rate (cpm),

$\bar{b}_1$ = average blank count rate (cpm), and

$\bar{b}_2$ = average background count rate (cpm).

Usually $\bar{b}_1$ and $\bar{b}_2$ are experimentally determined as a combined quantity.

K = factor to convert disintegration rate in disintegrations per minute (dpm) to curies. The value of K for different concentration expressions (C) is:

C	K
mCi/l	2.22×10^9
μCi/l	2.22×10^6
pCi/l	2.22

V = volume of sample in milliliters,

E = counting efficiency for the nuclide under the counting conditions specified for the determination. E is usually determined by analyzing standards in the same analytical procedure as for samples (a modified procedure is used in two methods described in this report),

f = fractional recovery of the nuclide in the sample,

λ = decay constant of the nuclide determined by: $\frac{\ln 2}{T_{1/2}}$,

where

$T_{1/2}$ = half-life of the nuclide of interest in the appropriate time units, and

t = elapsed time between collection of the sample and count of radioactivity (in same time units as used for λ).

The counting efficiency factor E, is calculated by the following general equation:

$$E = \frac{\bar{c}_n}{d_n f_n (e^{-\lambda t_n})}, \qquad (2)$$

where

$\bar{c}_n$ = average count rate of standard in cpm after correction for background and blank,

d_n = disintegration rate of standard (dpm),

f_n = fractional chemical recovery of the nuclide in the standard, and

t_n = elapsed time between certification of the standard and the count, in some units as the respective λ.

In the determinations of gross alpha and beta activity, cesium-137 and 134, tritium (without electrolysis), radium-228, radium as radium-226, and radium-226, the chemical recovery factors f and f_n are not determined. The product Ef_n is determined by counting the standard and is substituted for Ef in equation 1. This procedure is valid when f and f_n are equal and reproducible (within experimental limits) and effectively cancel out. The usual situation is that f and f_n are very close to unity.

Equations 1 and 2 apply when the sample and standard are counted under the same

conditions on the same detector. This is the normal situation. In the determination of radium-226 the individual samples and standards are counted in individual alpha scintillation cells each of which has its own counting efficiency (cell constant). Hence, in the determination of radium-226 an individual counting efficiency is determined for each cell.

In the determination of lead-210, radium-226, and radium-228, the radioactivity count is made on a relatively short-lived daughter of the nuclide determined. This necessitates the introduction of an "in-growth" or "build-up" factor, which is the fraction of the equilibrium concentration of daughter that had grown in at the time of separation from the parent nuclide. Since the daughter nuclides are relatively short lived with respect to the counting time, it is necessary to introduce a correction factor for decay during the counting interval. With radium-226 and radium-228 it is also necessary to introduce a factor that corrects for decay of the daughter during an aging period prior to counting.

Although a daughter nuclide is counted (in addition to the parent) in the determination of strontium-90, an in-growth factor is not used because the daughter is allowed to reach a constant level (99.5 percent of equilibrium) before counting.

The relationship of the three correction factors to the time intervals involved in the counting of a daughter nuclide is illustrated in figure 1. The figure shows growth and decay of the daughter with time and identifies the significant time intervals. The general equation for use with ingrown nuclides is:

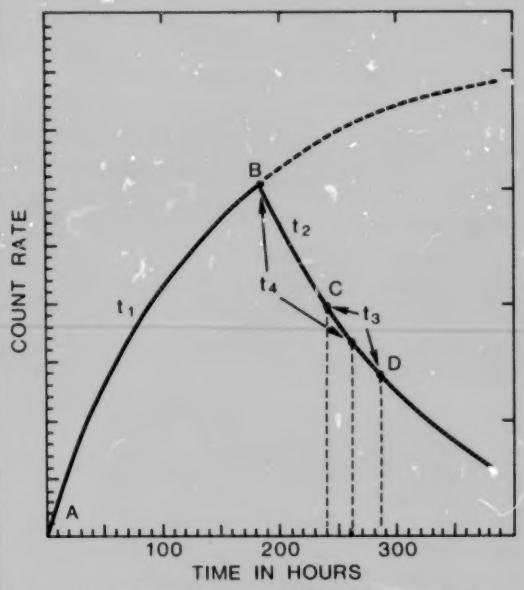
$$C = \frac{1000\bar{c}Z}{KV\varepsilon f(e^{-\lambda t})XY}, \qquad (3)$$

where

C = concentration of radionuclide. This is usually expressed in pCi/l.

$\bar{c}$ = average count rate of sample in cpm after correction for background and blank,

$X = 1 - e^{-\lambda t_1}$ (in-growth of daughter),



A-B IN-GROWTH OF DAUGHTER NUCLIDE IN TIME t_1
(NUCLIDE ILLUSTRATED HAS HALF-LIFE OF 3.82d)
B SEPARATION OF DAUGHTER FROM PARENT
B-C DECAY OF DAUGHTER BEFORE COUNTING. TIME INTERVAL t_2
C BEGINNING OF COUNT
C-D DECAY OF DAUGHTER DURING COUNTING INTERVAL t_3
t_4 TIME INTERVAL BETWEEN SEPARATION OF DAUGHTER FROM PARENT AND MIDPOINT OF COUNTING INTERVAL

Figure 1.—In-growth and decay of a daughter nuclide, significant time intervals.

$Y = e^{-\lambda_1 t_3}$ (decay of daughter between separation from parent and beginning of count),

$Z = \frac{\lambda_2 t_3}{1 - e^{-\lambda_1 t_3}}$ (decay of daughter during counting period),

where

λ = decay constant of parent nuclide,

t = elapsed time of parent between collection of the sample and separation of daughter,

λ_1 = decay constant of daughter nuclide,

t_1 = in-growth time of daughter, point A to B (fig. 1),
t_2 = delay before counting, point B to C. Separation of the daughter from the parent at time B, and
t_3 = time interval for counting of the daughter, point C to D.

K, V, f, and E are as defined for equation 1. The efficiency calculation for in-grown nuclides is:

$$E = \frac{\bar{c}_n}{d_n f_n (e^{-\lambda t_2}) XY}, \qquad (4)$$

with symbols and units as defined in equations 2 and 3.

Because of the short counting time permitted by the higher concentration of the standard, the counting time is short relative to the half-life. Hence the correction factor for decay during counting is eliminated.

The general equations are modified in accordance with specific conditions prevailing in the determination of individual radionuclides. For example, f and f_n are eliminated when chemical separations are not used or when the chemical recovery factor is included in the determination of overall efficiency. Decay terms are eliminated when the half-life of the nuclide permits.

The terms used in equations 1 to 4 are not repeated under the calculation section of the individual determinations unless required for clarification.

Glossary

Confidence level. The stated probability, under the experimental conditions employed, that the value will be within the interval indicated by the precision around the mean.

Decay. The spontaneous radioactive transformation of one nuclide into a different nuclide or into a different energy state of the same nuclide. Every decay process has a definite half-life.

Dissolved. The sample is filtered through a 0.45 micrometer membrane filter and the filtrate analyzed.

Filterable solids. Those dissolved solids capable of passing through a 0.45 micrometer membrane filter and dried to constant weight at 180°C.

Half-life. The time required for the decay of a given quantity of a radioactive substance to one-half its original mass; thus it is a measure of the rate of such processes.

Minimum detection level. The least amount or concentration that can be detected and quantified by a test method.

Nonfilterable solids. Those solids which are retained by a 0.45 micrometer membrane filter and dried to constant weight at 103°–105°C.

Precision. The degree of agreement of repeated measurements of the same property expressed in terms of dispersion of test results about the mean result obtained by testing of a homogeneous sample(s) under specific conditions.

Sorption. A general term for the processes of absorption and adsorption.

Selected references

Principles of radioactivity, nuclear instrumentation

Friedlander, G., Kennedy, J. W., and Miller, J. M., 1964, Nuclear and radiochemistry: New York, John Wiley and sons, 520 p.

Glasstone, S., 1958, Sourcebook on atomic energy: second edition, D. Van Nostrand Co., 525 p.

Hogerton, J. F., 1963, The atomic energy deskbook: New York, Reinhold Publishing Co., 623 p.

Overman, R. T., and Clark, H. M., 1960, Radioisotope techniques: New York, McGraw-Hill Book Co., 464 p.

Compilations of data on radioactivity and radiochemistry

Holden, N. E. and Walker, F. W., 1969, Chart of the nuclides: Schenectedy, N.Y., General Electric Co.

Lederer, C., Hollander, J. M., and Perlman, I., 1968, Table of isotopes: 6th ed., New York, John Wiley and Sons, 593 p.

National Academy of Sciences, National Research Council, 1960–62, A series of publications on radiochemistry of the elements beginning with NAS–NS publication no. 3001, The radiochemistry of cadmium: Revisions of publications on several elements have since been published.

U.S. Dept. of Health, Education and Welfare, Public Health Service, 1970, Radiological health handbook: 445 p.

Radioactivity in the environment

Adams, J.A.S., and Lowder, W. M., 1964, The Natural radiation environment: William March Rice University, University of Chicago Press, 1069 p.

Jacobs, D. G., 1968, Sources of tritium and its behavior upon release to the environment: U.S. Atomic Energy Commission TID–24635, 118 p.

Radioisotope methods in hydrology

International Atomic Energy Agency, Vienna, 1967, Guidebook on isotopic techniques in hydrology: 175 p.

——— 1970, Isotope hydrology (Latest in a series of symposia on isotopic techniques in hydrology. References to earlier symposia are given in the 1970 publication), 623 p.

Radiochemical analytical methods

Crouthamel, C. E., 1970, Applied gamma-ray spectrometry: second edition revised by Adams, F. and Dams, R., Oxford, Pergamon Press, 747 p.

Larrukhina, A. K,. Malysheva, T. V., Pavlotskaya, F. I., 1967, Chemical analysis of radioactive materials: Cleveland, CRC Press, a division of Chemical Rubber Co., originally published in Moscow, 360 p.

Wahl, A. C., and Bonner, N. A., 1958, Radioactivity applied to chemistry: New York, John Wiley and sons, 536 p.

Radioactivity regulations and safety

Federal Water Pollution Control Administration (now Environmental Protection Agency), 1968, Water quality criteria: 214 p.

General Safety Committee of the Manufacturing Chemists Assoc., 1954, Guide for safety in the laboratory: New York, Van Nostrand, 221 p.

International Atomic Energy Agency, Vienna, 1960, Safe handling of radioisotopes, health physics addendum: Safety series no. 2, 120 p.

——— 1962, Safe handling of radioisotopes: Safety series, no. 1, 159 p.

Morgan, K. Z., and Turner, J. E., 1971, Principles of radiation protection: New York, John Wiley and Sons, 598 p.

Saenger, E. L., 1963, Medical aspects of radiation accidents: AEC contract AT (30–1)– 2106 with University of Cincinnati, U.S. Atomic Energy Comm., 328 p.

U.S. Dept. of Commerce, National Bureau of Standards, 1951, Control and removal of radioactive contamination in laboratories: NBS Handb. 48, 24 p.

——— 1953, Maximum permissible amounts of radioisotopes in the human body and maximum permissible concentrations in air and water: Report of subcommittee 2 of the National Committee on Radiation Protection, NBS Handb. 52, 45 p.

——— 1959, Maximum permissible body burdens and maximum permissible concentrations of radionuclides in air and water for occupational exposure: Recommendations of the National Committee on Radiation Protection, NBS Handb. 69, 95 p.

U.S. Public Health Service, 1962, Drinking water standards, 1962: U.S. Public Health Service Pub. 956, 61 p.

U.S. Environmental Protection Agency, 1973, Water quality criteria, 1972: EPA-R3.-73.033, U.S. Govt. Printing Office, Wash. D.C., 594 p.

——— 1975, Interim primary drinking water regulations: Title 40, Code of Federal Regulations; Part 141, Federal Register, v. 40, no. 150, Aug. 14, 1975, 5 p.

U.S. Nuclear Regulatory Commission, 1976, Rules and regulations: Title 10, Chapter 1, Code of Federal Regulations—Energy, Part 20, Standards for protection against radiation, Sept. 1975, updated through April 19, 1976, 18 p.

References

Barker, F. B., Johnson, J. O., Edwards, K. W., and Robinson, B. P., 1965, Determination of uranium in natural waters: U.S. Geol. Survey Water-Supply Paper 1696–C, 25 p.

Begemann, F., and Libby, W. F., 1957, Continental water balance, ground-water inventory and storage times, surface ocean mixing rates and world wide circulation patterns from cosmic ray and bomb tritium, Geochim. Cosmochim. Acta 12, p. 277–296.

Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geol. Survey Techniques Water-Resources Inv., book 5, chap. A1, p. 4–15.

Chalov, P. I., Tuzova, T. A., and Musin, Ya. A., 1964, Isoptope ratio of U-234/U-238 in natural waters and utilization of the ratio in nuclear geochronology: Izv. Akad. Nauk. SSSR, Ser. Geofiz, no. 10 p. 1552–61.

Cherdyntsev, V. V., Orlov, D. P., Isabaev, E. A., and Ivanov, V. I., 1961, Isotopes of uranium in natural conditions, Radiokhimijia, no. 10, p. 840–848.

Cooper, J. A., Reicitelli, L. A., and Perkins, R. W., 1970, An anticoincidence-shielded Ge(Li) gamma-ray spectrometer and its application to radioanalytical chemistry problems: Jour. Radioanal. Chem. 6, 147–163 p.

Edwards, K. W., 1968, Isotopic analysis of uranium in natural waters by alpha spectrometry: U.S. Geol. Survey Water-Supply Paper 1696–F, 26 p.

Holtzmann, R. B., 1964, Lead-210 and polonium-210 in potable waters in Illinois, *in* The Natural Radiation Environment: Chicago, Univ. of Chicago Press, p. 227–238.

Jacobs, O. G., 1968, Sources of tritium and its behavior upon release to the environment: U.S. Atomic Energy Comm. TID–24685, 118 p.

Johnson, J. O., 1971, Determination of radium-228 in natural water: U.S. Geol. Survey Water-Supply Paper 1696–G, 26 p.

Kaufmann, S., and Libby, W. F., 1954, The natural distribution of tritium: Physical Review, v. 93, p. 1337–1344.

Krause, D. P., 1959, Ra-228 (Mesothorium I) in Illinois well waters: Argonne Nat. Lab. Radiol. Phy. Div. Semiannual Rept. ANL–6049, p. 51–52.

Libby, W. F., 1955, Radiocarbon dating, second edition: Univ. of Chicago Press, 124 p.

Nydal, R., 1966, Variations in carbon-14 concentration in the atmosphere during the last several years: Tellus 18, p. 271–275.

Patterson, R. L., and Lockhart, L. B., 1964, Geographical distribution of lead-210 in ground level air, *in* The Natural Radiation Environment: Chicago, Univ. of Chicago Press, p. 383–394.

Pearson, F. J., 1965, Use of C-13/C-12 ratios to correct radiocarbon ages of materials initially diluted by limestone: Internat. Conf. on Radiocarbon and Tritium Dating, 6th, Pullman, Washington, 7–11, June 1965, USAEC Conf. 650652, Proc., p. 357–366.

Rama, M. K., and Goldberg, E. D., 1961, Lead-210 in natural waters: Science, 134, p. 98–99.

Rona, Elizabeth, Gilpatrick, L. O., and Jeffrey, L. M., 1956, Uranium determination in sea water: Am. Geophys. Union Trans., v. 37, p. 697–701.

Scott, R. C., and Barker, F. B., 1959, Radium and uranium in ground water of the United States: Conf. on the peaceful uses of atomic energy, 2d, Geneva, Switzerland, 1958, Proc., v. 2, p. 154–157.

Starik, I. E., 1959, Principles of radiochemistry: Publishing house of the Academy of Sciences, USSR, Translation AEC–tr–6314, Office of Tech. Services, Dept. of Commerce, Washington, D.C. 20230.

Suess, H. E., 1965, Secular variations of the cosmic-ray produced carbon-14 in the atmosphere and their interpretations: Jour. Geophys. Res., 70(23), 5937–5952.

Thatcher, L. L., 1969, Principles of the application of nuclear techniques to hydrologic investigations, The progress of hydrology: First Internat. Seminar for Hydrology Professors, Univ. of Illinois, Urbana, Proc., p. 149–193.

Thurber, D. L., 1962, Anomalous U-234/U-238 in nature: Jour. Geophys. Research, v. 67, p. 4518–4520.

Wood, W. W., 1976, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geol. Survey Techniques Water-Resources Inv., book 1, chap. D2, (In press).

Carbon-14, dissolved, apparent age
Liquid scintillation method, Denver Lab (R-1100-76)

Parameter and code: Carbon-14, dissolved, apparent age (years): none assigned

1. Application

The method determines the apparent age of carbon-14 dissolved in the water sample. It is suitable for the analysis of any natural-water sample from which 5 g of dissolved carbon can be obtained. Only carbon in the form of dissolved CO_2 and its hydrolysis products is determined. The apparent age, determined by comparison with a standard of known age (see sec. 5.10), applies only to the carbon-14 in the sample; use of the determination to date the water itself requires a number of additional measurements and assumptions and a general knowledge of the geohydrologic system from which the sample was obtained. As noted below, a modification of the procedure is used for waters containing sulfate in excess of approximately 200 mg/l.

2. Summary of method

The method is based on that of Noakes and others (1967). Dissolved carbon in the carbonate system is concentrated from a large volume of water by precipitation of barium carbonate. The precipitate is treated with acid to liberate carbon dioxide, which is then allowed to react with metallic lithium to produce lithium carbide:

$$2CO_2 + 10Li \rightarrow Li_2C_2 + 4Li_2O.$$

The carbide is then hydrolyzed to produce acetylene:

$$Li_2C_2 + 2H_2O \rightarrow 2LiOH + C_2H_2.$$

Finally, the acetylene is passed over a vanadium-doped aluminum oxide catalyst to form benzene:

$$3C_2H_2 \rightarrow C_6H_6.$$

The benzene is placed in a tared scintillation counting vial, weighed, and then diluted slightly with a toluene solution containing a mixture of scintillators sensitive to low-energy betas. The activity of the sample is measured in a liquid scintillation counter. From the ratio of carbon-14 activity to the weight of carbon recovered, the apparent age of the carbon in the sample may be determined.

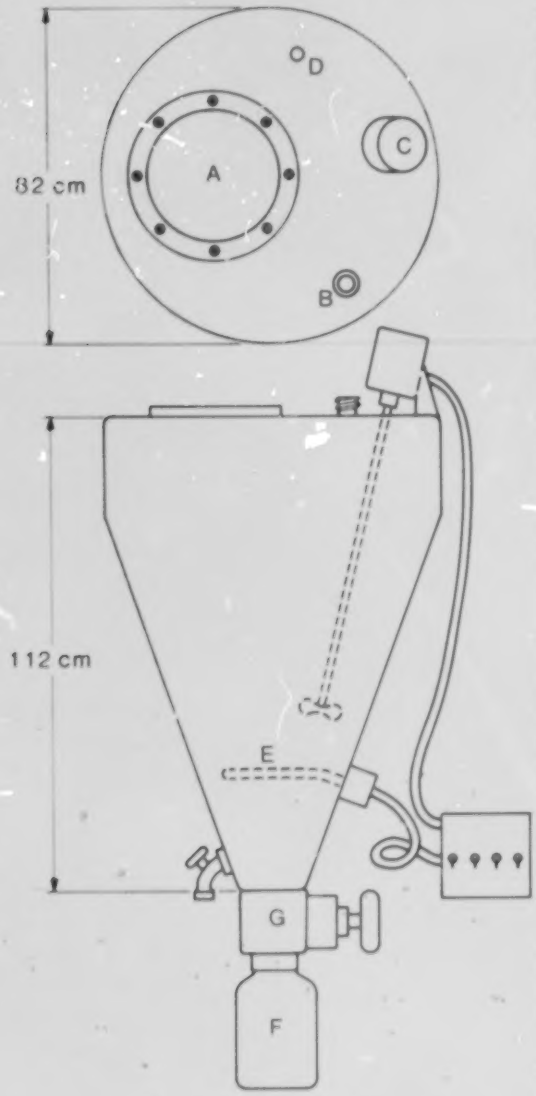
3. Interferences

The conversion from CO_2 to C_6H_6 is apparently free of both chemical and radiometric interferences. During sample collection and precipitation procedures interference may result from contact with the atmosphere or from dissolved sulfate concentrations in excess of approximately 200 mg/l.

The sample collection must minimize atmospheric contact with the water. Sample collection should be in a closed system from the sampling point to the collection containers. Collection containers (normally 15- to 55-gal steel drums) should be filled by inserting tubing to the container bottom, and flow continued until three container volumes have passed through the container. The sampling tube should be removed slowly and the container capped immediately after removal of the delivery tube.

4. Apparatus

4.1 *Beakers*, polyethylene, 400 ml.
4.2 *Cylinder*, graduated, 50 ml.



A - PLEXIGLASS VIEWING PORT
B - CONNECTOR FOR HOSE FROM SAMPLE BARREL
C - STIRRING MOTOR
D - PRESSURE RELIEF VALVE
E - IMMERSION HEATER
F - MASON JAR
G - GATE VALVE

Figure 2.—Apparatus for collection of carbonates from a water sample.

4.3 *Drums*, steel, 15-gal and 55-gal capacity with 1- and 2-inch bungs.

4.4 *Liquid scintillation counter.*

4.5 pH *indicating paper*, pH 2.0–5.0 range.

4.6 *Precipitator* for barium carbonate (fig. 2).

4.7 *Vacuum line* for storage of acetylene and conversion to benzene (fig. 3).

4.8 *Valves* for transfer of water sample from drums to precipitator.

5. Reagents

5.1 *Ascarite* (trade name of Arthur H. Thomas Co. for sodium hydroxide-impregnated asbestos).

5.2 *Barium chloride-lanthanum chloride solution*: Dissolve 290 g $BaCl_2 \cdot 2H_2O$ and 10 g $LaCl_3$ in distilled water and dilute to 1 liter.

5.3 *Benzene*, spectroscopic grade, free of carbon-14 activity.

5.4 *Catalyst*, vanadium-doped Al_2O_3, or Mobil Oil Co. Durabead.

5.5 *Dry ice.*

5.6 *Isopropanol*, technical grade.

5.7 *Liquid nitrogen.*

5.8 *Lithium metal*, shot, packed, and stored under argon.

5.9 *Nitrogen gas.* Must be free of CO_2 or scrubbed to remove CO_2.

5.10 *Oxalic acid.* National Bureau of Standards contemporary standard.

5.11 *Phosphoric acid*, concentrated (85 percent).

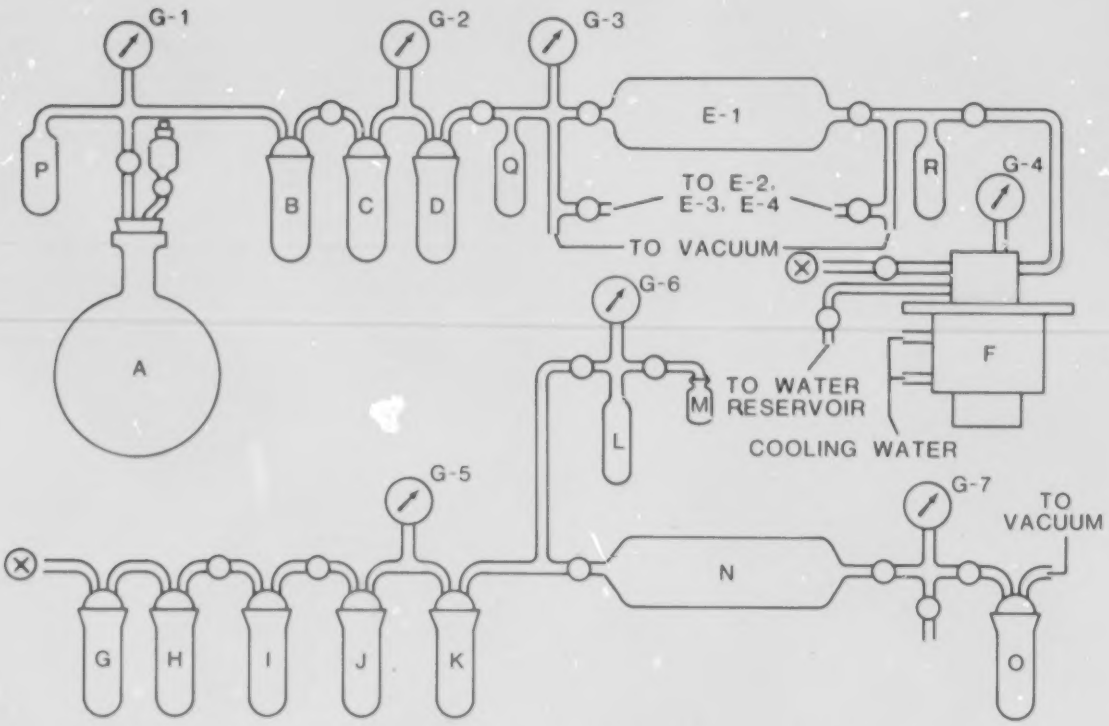
5.12 *Phosphorus pentoxide*, granular.

5.13 *Scintillator solution*: 10 g 2,5-diphenyloxazole (PPO), 0.25 g 1,4-bis-2-(4-methyl-5-phenyloxazolyl)-benzene (dimethyl POPOP). Dissolve in 250 ml analytical-grade toluene.

5.14 *Sodium hydroxide solution*, 5 *M*.

5.15 *Sulfuric acid*, 0.0164 *N*.

5.16 *Strontium chloride-lanthanum chloride* solution: Dissolve 230 g $SrCl_2 \cdot 2H_2O$ and 10 g $LaCl_3$ in distilled water and dilute to 1 liter.



A - CARBON DIOXIDE EVOLUTION FLASK
B, C, D, G, H, I, J, K, O - TRAPS
E-1 - E-4, N - GAS STORAGE CYLINDERS
F - REACTION CHAMBER
L - CATALYST REACTION TUBE
M - COLD FINGER FOR BENZENE
P, Q, R - COLD FINGERS
G-1 - G-7 - VACUUM GAUGES

Figure 3.—Vacuum line for preparation of acetylene and conversion to benzene.

6. Procedure

6.1 Determine the volume of water sample required to contain 5 g carbon as carbonate or bicarbonate. Alkalinity contributed by silicate, borate, phosphate, and other basic constituents is included in the following estimation of carbonate alkalinity. Therefore, the method underestimates the volume required if noncarbonate alkalinity is also present.

6.1.1 To 50-ml water sample in 400-ml beaker add 30 ml 0.0164 N sulfuric acid. Test the pH, using narrow-range indicating paper or a pH meter. If the pH is above 4.5, sufficient carbon is contained in 15 gal (55 liters) of the water sample.

6.1.2 If the pH is less than 4.5, add a second 50-ml portion of water sample to the solution in the 400-ml beaker. Again, test the pH. If the pH is now above 4.5, it is satisfactory to use two 15-gal drums of water sample. If the pH is still less than 4.5, repeat the addition of 50-ml sample aliquots to the 400-ml beaker until a pH of 4.5 is obtained. Collect one 15-gal drum for each 50-ml portion of sample required for neutralization of the acid to pH 4.5. Six 15-gal or two 55-gal drums is the maximum volume collected.

6.2 Collection of sample.

6.2.1 Fill each 15-gal drum by inserting a hose to the bottom of the drum and fill until two or more drum volumes have overflowed. Remove hose, insert plugs in bungs and tighten securely, taking care to minimize trapped air. Ship to the laboratory taking care to prevent freezing in cold weather.

6.3 Collect dissolved carbonate species by precipitation as barium carbonate using the precipitation apparatus shown in figure 2.

6.3.1 Attach a 2-liter Mason jar to the bottom of the precipitation cone. Run a hose from the 15-gal drum containing the sample to the precipitator. Seal the top plate and sweep out the unit with nitrogen gas to remove atmospheric carbon dioxide. Apply pressurized nitrogen to the 15-gal drum to force the water sample over into the precipitator.

6.3.2 Precipitate barium sulfate and carbonate by heating the sample with the immersion heater while stirring and adding 2 liters of barium chloride solution. If sulfate in the water sample exceeds approximately 200 mg/l (previously determined in the field or laboratory), strontium chloride is used as precipitant. Add 5 *M* sodium hydroxide slowly until pH of 10.4 is reached to convert bicarbonate to carbonate. Stir for 1 hr while holding the temperature at approximately 40°C.

6.3.3 Open the bottom valve and permit the barium sulfate-carbonate precipitate to flow into the Mason jar. Rotate stirring rod briefly by flipping control switch after 1 hr. Repeat cycle each one-half hour for next 2 hr. Major portion of precipitate should now be in the Mason jar. Close bottom valve, unscrew Mason jar, cap immediately, and seal exposed cap edges with vinyl or rubber tape.

6.4 Synthesis of benzene. The vacuum line for evolution of carbon dioxide and its conversion to benzene is shown schematically in figure 3.

6.4.1 Evolution of carbon dioxide from barium carbonate.

6.4.1.1 Decant most of the supernate from the barium sulfate-barium carbonate precipitate. Slurry the remaining precipitate and solution and transfer to a 4-liter heavy-walled Pyrex flask (A). Put a magnetic stirrer bar in the flask, cap with a two-hole stopper containing a separatory funnel, and place on the vacuum line. The vacuum line has been previously evacuated. Fill the separatory funnel with 125 ml of 85 percent phosphoric acid.

6.4.1.2 Evacuate the 4-liter flask carefully until bubbles foam in the slurry. Continue evacuation for 2 min.

6.4.1.3 Carefully run the phosphoric acid from the separatory funnel into the 4-liter flask. Carbon dioxide is released from the slurry. Allow the pressure to build up to approximately 120 mm of mercury (gauge G–1) and then open the stopcock to traps C and D so that pressure holds constant. Trap B is cooled with isopropanol-dry ice. Its function is to condense water. Traps C and D are cooled with liquid nitrogen, and their function is to condense carbon dioxide.

6.4.1.4 When the evolution of carbon dioxide is completed as shown by decrease of pressure on gauge G–1 to a constant minimum, carbon dioxide can now be transferred to the storage cylinders E–1, E–2, E–3, and E–4. The quantity of carbon dioxide is calculated from the known volume of each cylinder (slightly more than 6 liters) and the pressure on gauge G–3. Remove the liquid-nitrogen Dewar from trap C. Replace the liquid-nitrogen Dewar at trap D with an isopropanol-dry ice Dewar. Carbon dioxide flows into cylinder E–1 and when atmospheric pressure is reached, cylinder E–2 is opened and filled. The remaining two cylinders are successively filled in the same way.

6.4.1.5 Calculate the number of moles of carbon dioxide collected using volume of each storage cylinder, gauge pressure, and ambient temperature. Determine the grams of lithium metal to be used in the following carbide conversion step by multiplying the number of moles by 60.

6.4.1.6 Weigh out the required lithium shot, and place in the steel reaction chamber F. Evacuate the line and the chamber, start the flow of cooling water through the reaction chamber, and turn on the heater.

6.4.2 Reduction of carbon dioxide to lithium carbide carbide.

6.4.2.1 When lithium is a dull-red heat (as observed through the viewing port) admit carbon dioxide from the storage tanks into the reaction chamber F. Pressure drops sharply as the reaction proceeds (G–4). Con-

tinue heating until pressure drops to minimum. Continue heating for 1 hr. Turn off heat and allow to cool.

6.4.2.2 The lithium carbide containing carbon-14 is treated with water to form acetylene. Unreacted lithium reacts with water to produce hydrogen. Carefully introduce water from the distilled-water reservoir. The pressure rises because of production of acetylene and hydrogen. The acetylene condenses in traps I and K which are cooled with liquid nitrogen. Acetylene is purified before condensation by passage through traps G, H, and I. Traps G and H are cooled with isopropanol-dry ice and trap I contains ascarite and phosphorous pentoxide. One to 1.5 liter of water is required for complete reaction. When the pressure nears atmospheric, open the chamber to the vacuum pump to remove hydrogen as fast as it is produced. Continue pumping after completion of the reaction (bubbling ceases) until pressure falls to full vacuum.

6.4.3 Formation of benzene from acetylene.

6.4.3.1 The reaction tube L contains approximately 150 g of catalyst. Remove the liquid nitrogen Dewars from traps J and K and replace with isopropanol-dry ice coolant around K only. Place a liquid nitrogen Dewar around the cold finger M. Acetylene now sublimes from J and K and condenses in M.

6.4.3.2 Conversion of acetylene into benzene via the aluminum oxide catalyst averages about 97 percent with a good batch of catalyst. Occasionally an inferior batch is encountered, and conversion is much lower. There is no way to predict whether a new shipment of catalyst will give high or low conversion. The percentage of conversion for an individual run is determined by diverting the acetylene into storage cylinder N before it is frozen into cold finger M. The pressure reading shown on gauge G–6 and the known volume of N enables calculation of the moles of acetylene.

6.4.3.3 When acetylene is completely condensed in M transfer it to the catalytic reaction tube by replacing the liquid nitrogen Dewar with isopropanol-dry ice. Complete reaction is indicated by constant minimum pressure on gauge G–6. Complete reaction requires 2–3 hr. A second tube of catalyst may be required to achieve complete reaction.

6.5 Preparation for counting.

6.5.1 Transfer the catalyst tube containing benzene to a vacuum-distillation apparatus. Immerse the receiving tube in isopropanol-dry ice, and after the system is evacuated, heat the catalyst tube. When condensation of benzene in the receiving tube is complete, remove and weigh to determine benzene recovery.

6.5.2 Transfer 3.0 ml benzene to a scintillation-counting container, add 1.0 ml scintillator, and count under optimum conditions for carbon-14. Count each sample several times to accumulate at least 400 min of counting time on each sample. Reject early counting run results if instability is displayed.

7. Calculations

Calculate the apparent age of the sample from the following equation:

$$T = 3.32\, T_{\frac{1}{2}}\, (\log A_o - \log A),$$

where

T = apparent age of sample in years,
$T_{\frac{1}{2}}$ = half-life of carbon-14 in years (5,568 yr),
A_o = 0.950 times activity (in net counts per minute per gram of carbon) of NBS oxalic acid contemporary standard. This value is an average of several measurements on contemporary standards, and
A = activity of sample (in net counts per minute per gram of carbon).

8. Report

Report apparent age of dissolved carbon-14 in sample to nearest 50 yr for ages $<1{,}000$ and to nearest 100 yr for ages $>1{,}000$.

9. Precision

Precision as calculated from the counting variances for the sample, background, and

the standard counts give an optimistic estimation since possible errors involved in the precipitation of the carbon and its conversion to benzene are not included. According to Stuiver (1972), the precision of a carbon-14 date should be ±100 yr in the 10,000-yr range and ±800 yr in the 30,000-yr range.

References

Noakes, J. E., Kim, S., and Akers, L., 1967, Recent improvements in benzene chemistry for radiocarbon dating, Geochim. Cosmochim. Acta 31, (6) p. 1094–1096.

Stuiver, M., 1972, in Encyclopedia of geochemistry and environmental sciences, edited by Fairbridge, Van Nostrand Reinhold Co., p. 131.

Cesium-137 and cesium-134, dissolved
Inorganic ion-exchange method—gamma counting
(R-1110-76)

Parameters and codes: Cesium-137, dissolved (pCi/l): none assigned
Cesium-134, dissolved (pCi/l): 28410

1. Application

The combination of a reasonably specific ion-exchange separation of cesium isotopes with the energy discrimination available through gamma spectrometry provides a very specific method with potentially wide applicability. Boni (1966) applied the related KCFC technique to the determination of cesium-137 in milk, urine, seawater and freshwater. Petrow and Levine (1967) applied an ammonium hexacyanocobalt ferrate (NCFC) method to the determination of cesium-137 in precipitation.

2. Summary of method

The method is a development of Janzer, based on the work of Petrow and Levine (1967), who used NCFC for the concentration of cesium isotopes from water. The ammonium compound is superior to the potassium compound (KCFC) used by Prout, Russell, and Groh, (1965) because of elimination of background from potassium-40.

The gamma-counting technique begins with collection of radiocesium from relatively large volumes of water (up to 20 liters) by passing the sample through a column of inorganic ion-exchanger (NCFC). Several standards are prepared by passing a measured amount of standardized cesium-137 solution in water through columns prepared in the same manner as those used for the unknowns. The columns are dried and then counted using a well-type sodium iodide gamma detector and an automatic sample changer and single channel gamma spectrometer. The signal to noise ratio is optimized by adjusting the spectrometer window to the cesium-137 or cesium-134 energy peaks.

Blanks consisting of test tubes with exchanger are counted with the comparator standards and samples for a minimum of three 50-min counts. The cesium concentration is calculated on the basis of the net gamma counts observed in the standards and samples.

3. Interferences

Ruthenium, zirconium-niobium, cobalt, and zinc were reported to be sorbed by KCFC from neutral aqueous solutions. Sorption of interfering radionuclides was reduced to less than 0.1 percent from a 10 *N* HCl and 0.5 *N* HF solution (Boni, 1966). Boni also noted that interfering radionuclides could be removed by passing the sample through 50–100 mesh Bio-Rad Celex 100 in the calcium form before collecting the cesium on the KCFC.

Ellenburg and McCown (1968) reported iodine-131 and molybdenum-99 were sorbed in the analysis of reactor-fuel solutions using a slurry technique with 150 ml of sample and 50 mg of KCFC sorber. NCFC probably exhibits similar sorption. The degree to which extraneous radionuclides collected by NCFC may interfere during counting is a function of the energy resolution of the detector. Iodine-131 might interfere using the NaI de-

tector specified, because the cesium-137 photopeak at 662 keV might not be fully resolved from the iodine-131 photopeak at 636 keV. Using a Ge(Li) detector, there would be no interference because resolution would be complete. The combination of decay to eliminate molybdenum-99 ($T_{1/2}$=67 h) and other short-lived nuclides and high-resolution gamma spectrometry would appear to permit specific determination of cesium isotopes.

4. Apparatus

4.1 *Gamma spectrometer*, single-channel type.

4.2 *Glass and plastic tubing.*

4.3 *Glass wool.*

4.4 *Porous polypropylene disks:* Cut from 1.5 mm thick, 120 micrometer porous hydrophilic polypropylene sheeting (Bel Art F–1256 or equal).

4.5 *Sample changer*, automatic for 16 ×150-mm test tubes, coupled to a printout system.

4.6 *Slotted 16×150-mm test tubes:* A 2- to 3-mm vertical slot, 1-mm wide, is cut into the bottom of the test tube. Fire-polishing the tubes after cutting reduces breakage.

5. Reagents

5.1 *Ammonium hexacyanocobalt ferrate*, (NCFC) 30–60 mesh prepared after the manner described by Petrow and Levine (1967).

Add 10 ml of 0.5 *M* sodium ferrocyanide solution dropwise (approximately 35 ml/min) to 240 ml of 0.3 *M* cobalt nitrate-1.0 *M* ammonium nitrate solution while stirring on a magnetic mixer. Centrifuge slurry in 250-ml centrifuge tubes, decant, and discard the supernate.

Wash slurry with water several times to remove excess unreacted salts. Dry slurry in tubes by heating overnight in 80°C oven. Crush dried salt and sieve to collect 30–60 mesh fraction. Retain fines for incorporation with next batch of slurry prepared.

The measured cation exchange capacity for 30–60 mesh KCFC was reported by Prout, Russell, and Groh (1965) to range from 0.3 to 0.5 meq Cs/g KCFC using a cesium nitrate feed solution varying from 0.001 to 0.008 *M*. They calculated a theoretical exchange capacity of about 6 meq/g for KCFC.

5.2 *Cesium-137 and cesium-134 standard solutions:* Obtain from the National Bureau of Standards or other commercial suppliers. Dilute to approximately 100 pCi/ml for use.

6. Procedure

6.1 Using the slotted 16×150-mm test tubes, prepare exchange columns by placing small plug of glass wool in bottom of tube, add 30–60 mesh NCFC to a depth of 1 cm, and position a porous polypropylene disk on top of the NCFC to keep it in place. Do not compress the NCFC granules, or excessive flow reduction will result from the slight swelling which occurs when the sorber is wetted. Prepare columns as uniformly as possible to obtain reproducible counting geometry in the well-type detector.

6.2 Using 5-mm glass and plastic tubing, prepare a series of siphons which will provide a 1- to 1.5-meter head. Firmly insert the lower end of the siphon into the numbered test tube exchanger using a size 0, one-hole rubber stopper, and place the upper end of the siphon in the water sample. Maximum sample volume normally used is 20 liters.

6.3 Apply suction to the slot of the test tube to start flow. Flow rates of 1–5 ml/min are normal. More rapid flow rates can be obtained by using coarser NCFC or increasing the siphon head, but contact time would be reduced accordingly. Some color may be leached out of the NCFC during the first few milliliters of flow, but this apparently has no effect on the cesium collection.

6.4 When all the solution has passed through the column, disconnect the siphon, wipe the tubes dry, and place in a 30°C oven to dry.

6.5 Prepare several comparator standards by passing a measured amount of cesium-137 standardized solution (20–100 pCi) through additional exchanger tubes.

6.6 Adjust the gamma spectrometer to obtain optimum counting in the cesium-137

energy region (662 keV) or the cesium-134 energy region (605 keV, 796 keV).

6.7 Count reagent blanks, standards, and samples for a minimum of three 50-min counting periods each.

7. Calculations

7.1 Efficiency factors for cesium-137 (E_a) and cesium-134 (E_b) are calculated by the following equations. The efficiency factor includes counting efficiency and chemical recovery. Use of standard equation 2 to correct for cesium-137 decay is not often required.

$$E_a = \frac{\bar{c}_s}{d_s(e^{-\lambda_a t_s})},$$

$$E_b = \frac{\bar{c}_s}{d_s(e^{-\lambda_b t_s})},$$

where

$\bar{c}_s$ = average count rate of standard (cpm) corrected for background and blank,
d_s = disintegration rate of standard (dpm),
λ_a = decay constant of cesium-137 (0.02295 yr^{-1}),
λ_b = decay constant of cesium-134 (0.0280 $months^{-1}$), and
t_s = elapsed time between certification of the standard and the count, in same units as the respective λ.

7.2 Calculation of cesium-137 and cesium-134 concentrations: Use equation 1 where Ef is set equal to E_a or E_b. Decay correction for cesium-137 is usually not required.

$$\text{pCi/l of cesium-137} = \frac{1000\bar{c}}{KVE_a(e^{-\lambda_a t})}.$$

$$\text{pCi/l of cesium-134} = \frac{1000\bar{c}}{KVE_b(e^{-\lambda_b t})}.$$

8. Report

Report concentrations to one significant figure for concentrations between 0 and 10 pCi/l and to two significant figures for higher concentrations.

9. Precision

Precision of the method is estimated to be approximately ±20 percent.

References

Boni, A. L., 1966, Rapid ion-exchange analysis of radiocesium in milk, urine, sea-water and environmental samples: Anal. Chemistry, v. 38, no. 1, p. 89–92.

Ellenburg, E. J., and McCown, J. J., 1968, Rapid carrier-free method for the radiochemical determination of cesium-137: Anal. Letters, v. 1, no. 11, p. 697–706.

Petrow, H. G., and Levine, H., 1967, Ammonium hexacyanocobalt ferrate as an improved inorganic exchange material for determination of cesium-137: Anal. Chemistry, v. 39, no. 3, p. 360–362.

Prout, W. E., Russell, E. R., and Groh, H. J., 1965, Ion exchange absorption of cesium by potassium hexacyanocobalt (II) ferrate (II): Jour. of Inorg. Chem., v. 27, p. 473–479.

Radiocesium, dissolved, as cesium-137 Inorganic ion-exchange method—beta counting (R-1111-76)

Parameter and code: Radiocesium, dissolved, as cesium-137 (pCi/l): none assigned

1. Application

Application is possible when identification of individual cesium isotopes is not required and when interfering beta-emitting isotopes are in low concentration. Concentration limits for interfering isotopes have not been fully evaluated but would appear to be lower than for the gamma-spectrometry technique for cesium-137 and cesium-134, dissolved (inorganic ion-exchange method—gamma counting, R-1110-76). Until interferences are quantitatively evaluated, examination of each sample for possible interference is advised. Applications to samples where radiocesium is the principal source of radioactivity would appear to be safe.

2. Summary of method

In the beta-counting technique (Janzer, 1973) the same ion-exchanger (NCFC) is used to collect the cesium-137 and cesium-134 isotopes as in the gamma technique, but a simpler batch operation is made possible by the smaller volume of water used. One hundred milligrams of the ion-exchanger are stirred with the buffered water sample and then separated by filtration through a paper or membrane filter. This forms a uniform low-density disk deposit that is optimum for beta counting. Standards are prepared using the same technique. The sample and standard disks are counted in a low-background beta counter with anticoincidence shielding.

The method determines total dissolved radiocesium concentration because individual isotopes are not identified by this beta counting.

3. Interferences

No interferences have been found.

4. Apparatus

4.1 *Low-background counter*, an anticoincidence-type counter with 2-in. thin window flowing gas proportional detector preferably capable of measuring both alpha and beta activity simultaneously. (The Beckman Wide Beta or Low Beta counters or equivalent, with pulse height discriminating circuitry, are satisfactory.)

4.2 *Filter*, nitrocellulose membrane filters, 0.45-micrometer pore size, 47-mm diameter. A suitable filter holder assembly to facilitate vacuum filtration using the 47-mm filters is required. The perforated backup plate under the filter disk must be plastic rather than glass because of the hydrofluoric acid solution used. Millipore Sterifil XX-047-10 or equivalent is satisfactory.

4.3 *Teflon, polyethylene, polypropylene, or other acid resistant beakers*, 600-ml volume.

5. Reagents

5.1 *Ammonium hexacyanocobalt ferrate (NCFC)*: Prepare as described by Petrow and Levine (1967), and sieve to collect the 30-60 mesh fraction.

5.2 *Cesium-137 standard solution.* Obtain from NBS or use commercial standards, approximately 100 pCi/ml.

6. Procedure

6.1 Place a 500-ml water sample in a plastic beaker.

6.2 Acidify with concentrated hydrochloric acid to 1 *N* and with hydrofluoric acid to 0.5 *N*. For a 500-ml sample, this requires 45 ml of concentrated hydrochloric and 10 ml of concentrated hydrofluoric acid.

6.3 Add 100 mg (±1 mg) of 30–60 mesh NCFC, and stir for 10 min. After allowing the NCFC to settle, decant the supernatant solution and filter it through a 0.45-micrometer membrane filter (47-mm diameter) in a vacuum-filtration assembly. With the last portion of liquid remaining in the beaker, transfer the NCFC to the filter taking care to obtain even distribution. Return the filtrate to the plastic beaker. Filter through the original filter disk a second time, and quantitatively transfer any remaining NCFC to the filter disk with small amounts of distilled water. Rinse down the funnel sides, and carefully wash the filter and retained NCFC several times so that the filter pad is not disturbed and a uniform deposit is maintained.

6.4 Mount the filter disk in a ring holder, and dry under an infrared lamp. Cover the dry material with a small sheet of plastic wrap (kitchen-type).

6.5 Count in the anticoincidence beta counter. Three 50-min counts for each sample are usually adequate.

6.6 Prepare standards in triplicate. Add 5.0 ml of 100 pCi/ml standard cesium-137 solution to 500 ml of distilled water, and carry out the analytical procedure exactly as with a sample. The standards prepared in this way are also covered with plastic film and may be retained for semipermanent use. If different sample sizes are used, corresponding standards should be prepared.

6.7 Prepare blanks by running the determination on 500 ml of distilled water.

6.8 Count the blanks and standards in the same way as the samples.

7. Calculations

7.1 The cesium-137 efficiency factor (E) includes chemical recovery and counting-efficiency corrections and is determined by equation 2 simplified by treating standards and samples the same so that no factor f is calculated. The following equation is then used:

$$E = \frac{\bar{c}_n}{d_n(e^{-\lambda t_n})}.$$

7.2 Calculation of cesium-137 concentration: Use general equation 1 simplified by eliminating the f term. Decay correction is seldom required.

$$\text{pCi/l of cesium-137} = \frac{1000\bar{c}}{KVE(e^{-\lambda t})}.$$

8. Report

Report cesium-137 activity to one significant figure below 10 pCi/l and to two significant figures above 10 pCi/l. The minimum concentration reported is that which represents two standard deviations above background. This is approximately 1 pCi/l with a 500-ml sample and a Beckman Low Beta counter or equivalent.

9. Precision

On the basis of limited data the analysis appears to be reproducible to ±10 percent at concentrations above 10 pCi/l with inferior reproducibility at lower concentrations.

Reference

Janzer, V. J., 1973, A rapid method for the determination of radioactive cesium isotopes in water: U.S. Geol. Survey Jour. Research, v. 1, p. 113–115.

Gross alpha and beta radioactivity, dissolved and suspended
Residue method (R-1120-76)

Parameters and codes: Gross alpha, dissolved as U natural (µg/l): 80030
Gross alpha, suspended, as U natural (µg/l): 80040
Gross alpha, suspended, specific activity as U natural (µg/g): 01518
Gross beta, dissolved, as cesium-137 (pCi/l): 03515
Gross beta, dissolved, as strontium-90/yttrium-90 (pCi/l): 80050
Gross beta, suspended, as cesium-137 (pCi/l): 03516
Gross beta, suspended, as strontium-90/yttrium-90 (pCi/l): 80060
Gross beta, suspended, specific activity as cesium-137 (pCi/g): 03518

1. Application

The method is applicable to any natural-water sample. Because of restrictions on the weight of residue which can be accommodated, the sensitivity falls off with increasing concentrations of dissolved solids.

2. Summary of method

The method is an extension of the procedure published by Barker and Robinson (1963) for gross beta radioactivity.

A representative aliquot, but not more than 1 liter of the sample including suspended solids, is filtered through a tared 0.45-micrometer membrane filter. The filter and retained solids are dried at room temperature and then at 105°C, cooled, and reweighed to determine the weight of nonfiltrable residue per liter.

A filtered volume of the sample containing no more than 150 mg of dissolved solids is evaporated to dryness in a Teflon evaporating dish. The residue is transferred to a tared, 2-in. concentric-ring, stainless-steel planchet, dried in a desiccator, weighed, and counted on a low-background alpha-beta counter. The observed radioactivity is compared with the activity of natural uranium and strontium-90/yttrium-90 and cesium-137 calibration standards, and results are reported relative to these reference isotopes. Thus, the measured sample activity is reported in terms of the amount of natural uranium and equilibrium strontium-90/yttrium-90 and cesium-137 activity which would give the same alpha and beta count rates respectively for the same weight of residue. The gross activities are reported in terms of equivalent quantities of reference standards of the true alpha and beta activities of the sample.

The accuracy of these approximations depends on a number of variables related to the energy distributions of the alpha and beta particles and the similarity of the residues used in preparation of the calibration curves to the actual sample residue. The method must be regarded as a rapid, semiquantitative measure of gross sample activity.

3. Interferences

Within its intended purpose, the method is free of interferences, although the accuracy varies considerably with the nature of the alpha and beta emitters, chemical composi-

tion of the sample, and uniformity of planchet preparation.

4. Apparatus

4.1 *Evaporating dishes*, Teflon, 100 ml.

4.2 *Hotplate* or steam table.

4.3 *Infrared drying lamps.*

4.4 *Low-background counting equipment.* Proportional counters capable of measuring both alpha and beta activity are desirable (for example, Beckman Instrument Co. Wide-Beta or Low-Beta II, or equivalent).

4.5 Membrane *filters*, 47-mm diameter, 0.45-micrometer pore size, cellulose nitrate or acetate type.

4.6 *Planchets*, stainless steel, 2-in. diameter, concentric-ring type.

4.7 *Specific conductance meter.*

4.8 *Vacuum desiccator.*

4.9 *Vacuum-filtration apparatus*, for 47-mm membrane filters.

5. Reagents

5.1 *Calibration solution* A: Dissolve 0.284 g $MgSO_4 \cdot 7H_2O$, 0.070 g NaCl, 0.026 g $CaSO_4 \cdot 2H_2O$, 0.109 g $NaHCO_3$, and 0.245 g $CaCO_3$ in distilled water, bubbling CO_2 gas through the solution if necessary to obtain clear solution. Dilute to 2.00 liters.

5.2 *Calibration solution* B: Dissolve 1.350 g $MgSO_4 \cdot 7H_2O$, 3.510 g NaCl, 1.550 g $CaSO_4 \cdot 2H_2O$, 0.508 g $MgCl_2 \cdot 6H_2O$, and 0.300 g $CaCO_3$ in distilled water, using CO_2 bubbling as necessary to dissolve. Dilute to 2.00 liters.

Note: Composition of the calibration solutions should approximate that of the samples to be analyzed. Solutions A and B were selected to approximate the composition average of 12 major rivers in the United States.

5.3 *Cesium-137 standard solution*, approximately 500 pCi/ml and acidified to approximately 1 *N* with hydrochloric acid.

5.4 *Hydrofluoric acid*, 49 percent.

5.5 *Strontium-90/yttrium-90 standard solution*, approximately 500 pCi/ml combined activity and acidified to approximately 1 *N* with hydrochloric acid.

5.6 *Uranium standard solution*, 1.00 ml = 100 μg U: Dissolve 0.1773 g of $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ in approximately 500 ml distilled water. Add 15 ml concentrated HNO_3 and dilute to 1,000 ml in a volumetric flask. Store in a Teflon bottle.

6. Procedure

6.1 Preparation of beta calibration curve.

6.1.1 Add the following amounts of calibration solutions A and B to 100-ml Teflon evaporating dishes:

Dish No.	A (ml)	B (ml)	Approx. residue wt. (mg)
1	25		10
2		5	20
3	80		30
4		10	40
5	140		50
6		20	60
7	200		70
8		25	80
9	250		90
10		30	100
11	300		110
12		35	120
13	350		130
14		40	140
15	400		150

To each dish and to four additional 100-ml Teflon evaporating dishes (Nos. 16, 17, 18, and 19) add 1.00 ml of strontium-90/yttrium-90 standard solution. To dishes 18 and 19 also add 5 drops concentrated NH_4OH.

6.1.2 Evaporate all the solutions to dryness on a low-temperature hotplate. When dishes 18 and 19 are dry, raise heat to approximately 350°C to volatilize NH_4Cl.

6.1.3 Perform steps 6.6 through 6.11 of the procedure which follows.

6.1.4 Plot the beta efficiency (net counts per minute per picocurie) against the residue weight to obtain the beta calibration curve.

6.1.5 Prepare a beta calibration curve for cesium-137 following steps 6.1.1 through 6.1.4. Use 1.00 ml of cesium-137 standard.

6.2 Preparaion of alpha calibration curve: The alpha calibration curve is obtained in exactly the same manner as the beta curve (step 6.1) except that 100 μg of uranium (1 ml of uranium standard solution) is substituted for the strontium-90/yttrium-90 beta

standard. It is important that the uranium standard be in secular equilibrium with respect to uranium-234. The uranium isotopes ratio may be determined by the method described elsewhere in this manual.

6.3 Sample analysis: Measure the specific conductance of each water sample. Multiply the specific conductance in μmhos/cm at 25°C by 0.65 to obtain an approximate value for the dissolved-solids concentration of the sample in mg/l. Determine the volume of sample which will contain approximately 100 mg of dissolved solids:

$$\text{Sample volume, } V\,(\text{l}) = \frac{100\ \text{mg}}{\text{mg/l}}.$$

The actual sample residue should weigh between 50 and 130 mg.

6.4 Gross radioactivity of the suspended solids is determined as follows: Vigorously agitate the sample bottle containing the total amount of sample collected and quickly pour off 1 liter of sample with suspended solids into a graduated cylinder. Allow sediment to settle and then, using suction, filter through a tared membrane filter. When only 100 ml of sample remains to be filtered, swirl to suspend solids and add suspension to filter funnel. Any remaining traces of sediment may be transferred using small amounts of distilled water.

6.5 Carefully rinse solids with a small amount of distilled water, and maintain as uniform a deposit as possible. Remove filter, allow to air-dry, and weigh. If the weight of solids is in excess of 150 mg, refilter a fresh aliquot of appropriate volume to obtain less than 150 mg, weigh, dry at 105°C, and count for alpha and beta radioactivity.

Although not totally comparable, the same absorption or counting efficiency factors for the respective counting instruments are used as for dissolved solids, and the calculations are made in the same way. The weight of suspended solids per liter of sample is also reported (USGS parameter code 00530) and may be used to calculate the radioactivity associated with the total weight of suspended solids per liter of original sample. Specific activity of the solids in pCi/g of suspended solids for the equivalent strontium-90/yttrium-90 or cesium-137 may also be calculated.

6.6 Gross radioactivity of the dissolved solids is determined as follows: Using a tared Teflon dish, evaporate the required volume of water to dryness on a hotplate or steam bath. Remove Teflon dishes from hotplate as soon as they reach dryness to prevent warping of dishes due to excess heat.

6.7 Determine approximate weight of residue by weighing dish plus residue and subtracting tare weight. If the weight of residue falls outside the 50- to 130-mg range, start a new evaporation using a larger or smaller sample volume as required.

6.8 Quantitatively transfer the residues in the evaporating dishes to tared planchets using rubber policemen and a minimum amount of distilled water to effect the transfers. Confine the solution and residue to the three inner concentric rings of the planchet during the transfer.

6.9 Dry the planchets under infrared heat lamps. Police down the evaporating dishes with small additional amounts of distilled water and transfer to planchets.

6.10 Repeat step 6.6. If a residue remains in the evaporating dish after three washes with distilled water, add a small amount of hydrofluoric acid, and use for a final policing.

6.11 Disperse the final liquid slurry in the planchets as uniformly as possible, using a stirring rod to disrupt large aggregates. Again evaporate to dryness.

6.12 Place the planchets in a vacuum desiccator and evacuate to complete the drying; weigh the planchets and determine the weight of residue.

6.13 Count the planchets in a low-background alpha-beta counter. Obtain three 50-min counts on each sample.

7. Calculations

Determine the equivalent concentration of alpha and beta emitters in each planchet from the net measured activity and the appropriate factor from a table of calibration curves.

$$\text{Gross } \alpha = \frac{Scpm\alpha}{F_\alpha} \times \frac{1000}{V_a} = \mu g/l \text{ as U natural,}$$

$$\text{Gross } \beta = Scpm\beta \times \frac{F_\beta \cdot 1000}{V_a}$$

$$= \text{pCi/l as } Sr^{90}/Y^{90} \text{ or as } Cs^{137},$$

where

$Scpm\alpha$ = alpha count rate of sample in counts per minute,

$Scpm\beta$ = beta count rate of sample in counts per minute,

F_α = alpha factor in cpm/μg of natural U,

F_β = beta factor in picocuries per count per minute, and

V_a = aliquot used in milliliters

8. Report

Report values of less than 1 pCi/l to one significant figure. Report higher values to two significant figures.

9. Precision

Results for a particular sample are usually reproducible to about ±20 percent at the 95-percent confidence level.

Reference

Barker, F. B., and Robinson, B. P., 1963, Determination of beta activity in water: U.S. Geol. Survey Water-Supply Paper 1696–A, 32 p.

Lead-210, dissolved
Chemical separation and precipitation method (R-1130-76)

Parameter and code: Lead-210, dissolved (pCi/l): none assigned

1. Application

The method may be used with all natural waters where detection of lead-210 with sensitivity to 2 pCi/l is acceptable. Where improved sensitivity is required, a larger sample than the normal 500 ml is concentrated by evaporation before beginning the procedure. Rama and Goldberg (1961) reported they were able to achieve sensitivity to 0.02 pCi/l by use of a 20-liter sample and direct precipitation of lead chromate from this large volume.

Lead recovery may be low in waters containing high concentrations of organic material that can possibly complex lead.

2. Summary of method

The analytical method is designed to isolate lead-210 in a relatively pure lead chromate precipitate. This is allowed to age to produce bismuth-210, a beta emitter with 5-d half-life. Lead-210 is not counted directly because of its very soft beta radiations of 15 and 61 keV, which are greatly attenuated by absorption. The bismuth isotope decays by beta emission with a beta maximum energy of 1.16 MeV, and these beta particles are easily counted.

3. Interferences

Henry and Loveridge (1961) have shown that essentially complete separation from radioisotopes of antimony, cesium, cobalt, iodine, phosphorous, ruthenium, strontium, thallium, zinc, and zirconium is achieved. Radium, thorium, uranium, potassium-40, and other natural radionuclides do not interfere. Lead-212 does not interfere because of the short half-life (10.6 hr). Stable lead in the water sample should cause no interference by increased beta absorption since lead concentrations seldom exceed a few tenths of a milligram per liter. A problem might be encountered with industrial wastes where lead concentrations could be much higher.

The application of the method to liquid waste should be checked by "spiking" samples with known lead-210 and determining percentage of recovery.

4. Apparatus

4.1 *Centrifuge*, capable of handling 50-ml tubes.

4.2 *Centrifuge tubes*, polypropylene, approximately 50-ml capacity.

4.3 *Copper disks*, 49-mm diameter, minimum thickness 0.1 mm.

4.4 *Ion-exchange columns*, 1-cm inside diameter, 10-cm long with 50-ml reservoir at top.

4.5 *Low-background counter*, an anticoincidence-type counter with 2-in. thin window flowing gas proportional detector preferably capable of measuring both alpha and beta activity simultaneously.

4.6 *Magnetic stirrer-hotplate.*

4.7 *Membrane filters*, 47-mm diameter, 0.45-micrometer pore size. Must be inert to warm, dilute chromic acid.

4.8 *Planchets*, stainless steel, 5-cm diameter.

4.9 *Tape*, cellulose, 5-cm wide roll, adhesive on both sides.

4.10 *Tape*, "Magic Tape" (Minnesota Mining and Manufacturing Co.), 8 mg/cm² density, 5-cm width.

4.11 *Vacuum-filtration* apparatus, for 47-mm membrane filters.

5. Reagents

5.1 *Acetic acid*, 25 percent by volume: Dilute 1 volume glacial acetic acid with 3 volumes distilled water.

5.2 *Ammonium persulfate.*

5.3 *Hydrochloric acid*, 8 *N* and 2 *N*.

5.4 *Ion-exchange resin*, Bio-Rad Ag1–X8, or equivalent, 50–100 mesh.

5.5 *Lead carrier solution*, 1 ml = 4.00 mg Pb^{+2}: Dissolve 6.394 g anhydrous $Pb(NO_3)_2$ in 100 ml of 1 *N* HNO_3 and dilute to 1,000 ml with distilled water.

5.6 *Lead-210 standard solution.* Suitable standards are available from Amersham/Searle Corp., Arlington Heights, Ill. Solutions must be kept strongly acidic (about 1 *N* in HNO_3) when dilutions are made.

5.7 *Nitric acid*, 0.01 *M:* Dilute 0.1 ml of concentrated HNO_3 to 120 ml.

5.8 *Nitric acid*, 0.001 *M:* Dilute 20 ml of 0.01 *M* HNO_3 to 200 ml.

5.9 *Potassium dichromate solution*, 4 percent: Dissolve 40 g reagent-grade $K_2Cr_2O_7$ in distilled water and dilute to 1 liter.

5.10 *Sodium acetate solution*, 10 percent: Dissolve 100 g anhydrous $NaC_2H_3O_2$ in distilled water and dilute to 1,000 ml.

5.11 *Sodium carbonate solution*, 1.25 *M:* Dissolve 265 g of anhydrous Na_2CO_3 in distilled water and dilute to 2,000 ml.

5.12 *Sodium sulfate*, anhydrous.

5.13 *Strontium carrier solution*, 1 ml = 60 mg Sr^{+2}: Dissolve 145 g $Sr(NO_3)_2$ in distilled water; add 1 ml concentrated HNO_3 and dilute to 1,000 ml.

5.14 *Surfactant*, Dade Aerosol OT, Scientific Products Co.

6. Procedure

6.1 Preparation of ion-exchange columns.

6.1.1 Slurry 4.0 g of ion-exchange resin with 10 ml of 8 *N* HCl in a 50 ml beaker. Cover and place in an ultrasonic cleaner for 1 min and allow to stand for at least 20 min.

6.1.2 Plug the end of the column with a small piece of glass wool, and wash with 8 *N* HCl.

6.1.3 Transfer the resin slurry completely to the column, allow to drain and settle.

6.1.4 Place a small glass-wool plug at the top of the resin column. Avoid packing the resin. Wash with 10 column-volumes each of 8 *N* HCl, distilled water, and finally 2 *N* HCl. The column is now ready for use. The resin is discarded after one use.

6.2 Preparation of lead-210 standard planchets: Three or more "permanent" standards are prepared by precipitating a known amount of lead-210 as lead chromate.

6.2.1 Add 5 ml of lead carrier solution and an accurately known amount of lead-210 (approximately 200 pCi is convenient) to 50 ml of 0.001 *M* nitric acid. Heat to 95°C, slowly add 5 ml of 4 percent potassium dichromate solution, stir for several minutes, and digest on a hotplate for 20 min with occasional agitation.

6.2.2 Cool to room temperature, filter through a tared 0.45–micrometer membrane filter, and wash the precipitate with a small amount of distilled water containing a few drops of aerosol OT solution.

6.2.3 Allow the membrane and precipitate to air-dry, then weigh and calculate the chemical yields. Mount the standards as described in step 6.16.

6.2.4 Allow the standards to age until the count rate becomes constant. This will require 40 d (8 half-lives of bismuth-210) or less, because 75 to 100 percent of the bismuth-210 coprecipitates with the lead chromate.

6.3 Analysis of the water samples: Measure a 500-ml water sample into an 800-ml beaker, add a magnetic stirring bar and a few drops of methyl orange indicator, and place on a magnetic stirrer-hotplate.

6.4. While stirring, add 0.01 *M* nitric acid dropwise until the indicator turns red. If the sample is initially acid to methyl orange, bring to color change with ammonia, then back to acid side with nitric acid. Add 5 ml of lead carrier solution, 4.5 g of anhydrous

sodium sulfate, and 1 g of ammonium persulfate. Cover with a watch glass, and heat and stir at the incipient boiling point for 1 hr.

6.5 Add 5 ml of strontium carrier solution to the sample and continue heating while stirring at the incipient boiling point for 20 min; retrieve the magnet, remove the beaker from the hotplate, and allow the precipitate to settle and solution to cool slowly to room temperature.

6.6 Decant or syphon off as much of the supernatant liquid as possible without disturbing the precipitate. Wash the residue into a 50-ml round-bottom Teflon or polypropylene centrifuge tube using a small volume of distilled water. Centrifuge, and discard the supernate.

6.7 Place a ½-in. Teflon-coated magnet in the centrifuge tube, add 40 ml of hot 1.25 *M* sodium carbonate solution, and place the tube in a boiling-water bath on a magnetic stirrer-hotplate. Stir vigorously for 20 min.

6.8 Remove the tube from the bath, and wash down any precipitate on the upper part of the tube using a jet of 1.25 *M* Na_2CO_3. Centrifuge and decant or syphon off most of the supernate. Syphoning is preferable because of the difficulty of decanting without disturbing the precipitate with the magnetic stirrer.

6.9 Repeat steps 6.7 and 6.8 two more times. Remove the stirring bar before the final centrifugation. Discard the final supernatant liquid.

6.10 Dissolve the lead-strontium carbonate precipitate in the centrifuge tube by cautiously adding 15.0 ml of 2 *N* HCl followed by 1.0 ml of 8 *N* HCl. Mix thoroughly and pour the solution onto the ion-exchange column. Be sure the flow rate does not exceed 2 ml/min.

6.11 Rinse the centrifuge tube with two 2-ml portions of 2 *N* HCl, adding these rinse solutions to the column.

6.12 Wash the column with a volume of 2 *N* HCl equal to two column-volumes plus the holdup volume in the column below the resin bed. Elute with 30 ml of distilled water, collecting the eluate in a 150-ml beaker. Record the date and time of elution. This fraction contains lead-210 free of daughter activity.

6.13 Add 3 ml of 25 percent (v/v) acetic acid and 5 ml of 10 percent sodium acetate to the eluate, and dilute to approximately 75 ml. Heat to incipient boiling and add slowly 5 ml of 4 percent potassium dichromate solution. Mix thoroughly by swirling the beaker and hold near the boiling point for 20 min with occasional swirling.

6.14 Remove the beaker from the hotplate and filter, while warm, through a tared 0.45-micrometer, 47-mm-diameter membrane filter. Rinse with distilled water, containing a few drops of Aerosol OT solution, to prevent the precipitate from clinging to the filter funnel.

6.15 Remove the filter membrane from the filtration apparatus, place on a clean surface, and allow to air-dry. Weigh the filter to determine chemical recovery.

6.16 Place the filter in the center of a 49-mm copper disk, the surface of which has been covered with a strip of double-faced cellulose tape. Cover the filter disk with a strip of 5-cm "Magic Tape," trim to the size of the copper disk, and place in a 5-cm planchet.

6.17 After an aging period of 7 d (or longer), count the samples in a low-background beta counter with a 5-cm detector for 100 min to attain sensitivity to 2 pCi/l. Extended counting improves the detection. For example, detection to 0.7 pCi/l is possible with a 1,000-min count.

7. Calculations

7.1 Lead-210 efficiency factor (E) and chemical recovery factor (f_s): Although bismuth-210, daughter of lead-210, is actually counted, an in-growth factor is not used in the determination of E. The standard is allowed to reach equilibrium (40-d standing) before counting, and the disintegration rate at this time is controlled by the lead-210 concentration. Determine f_s from the weight of lead chromate. E is determined using equation 2.

$$E = \frac{\bar{c}_s}{d_s f_s (e^{-\lambda_s t_s})}. \quad (2)$$

7.2 Calculation of lead-210 concentration: An in-growth factor is used in calculation of concentration in individual samples because the aging time before counting (approximately 7 d) is insufficient to attain equilibrium. The in-growth factor for each sample is obtained from a curve of the growth of activity with time (fig. 4) or, more accurately, by calculation. Chemical recovery factor is determined from the ratio of actual weight of lead chromate recovered to the theoretical weight. For 20-mg lead carrier, the theoretical weight is 31.20 mg of lead chromate. Use equation 3 with the terms for decay of daughter before counting and decay during counting eliminated. Calculate lead-210 concentrations using the equation below, and correct for decay if excessive time elapsed between the sample collection and analysis.

$$\text{pCi/l of lead-210} = \frac{1000\,\bar{c}}{VEf\,(e^{-\lambda t})\,(1-e^{\lambda t_i})},$$

where

$\bar{c}$ = net count rate of sample after correction for background and blank

λ = decay constant of lead-210 (0.0315 yr^{-1}),

t = elapsed time between collection of sample and analysis,

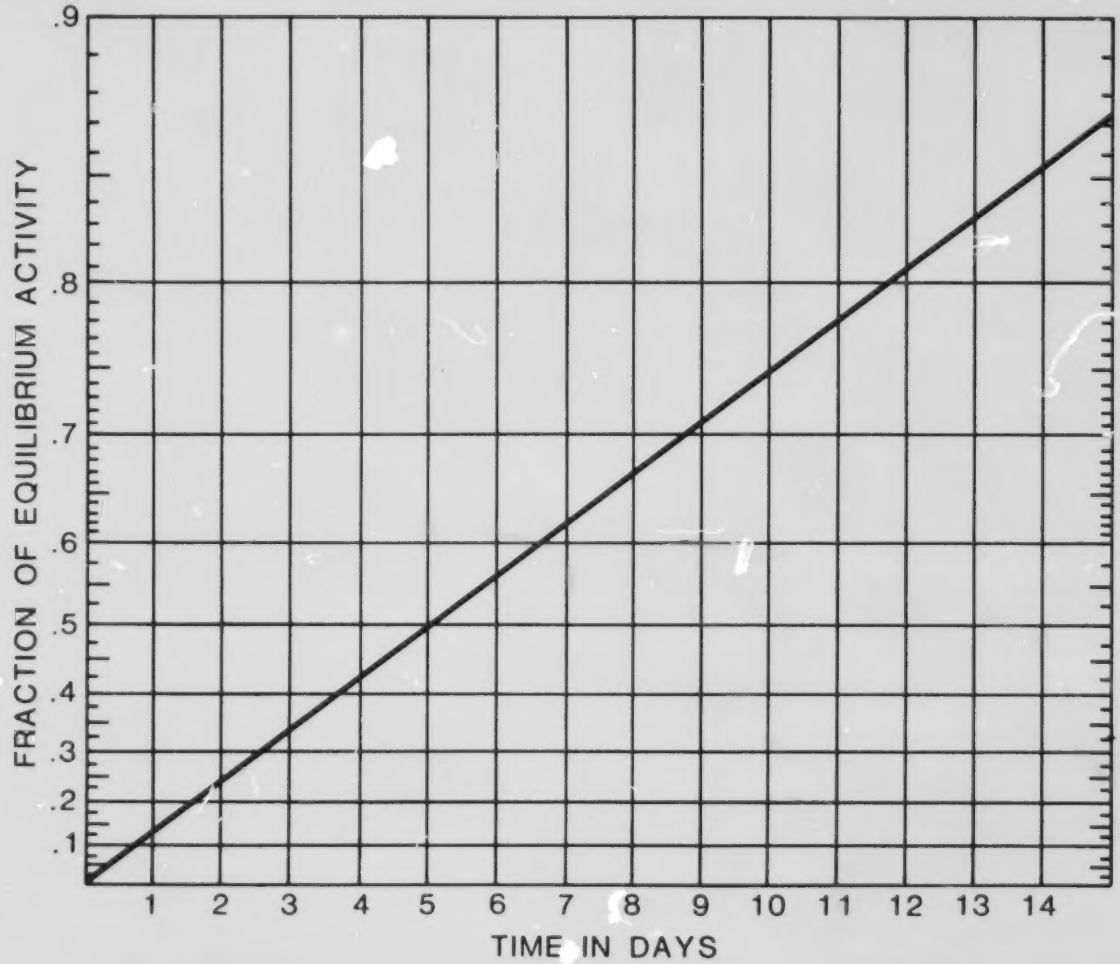


Figure 4.—Growth of bismuth-210 from pure lead-210 source.

λ_1 = decay constant of bismuth-210 (0.1384 d^{-1}),
t_1 = elapsed time between elution of the ion-exchange column (step 6.12) and counting, and
V, E, and f are as defined in equation 1.

8. Report

Report concentrations of less than 1 pCi/l to the nearest pCi/l; higher concentrations to two significant figures.

9. Precision

Tests with eight water samples to which known lead-210 was added gave recoveries averaging 98 percent with a mean deviation of ±2 percent at concentrations above 15 pCi/l. At lower concentrations the precision is ±2 pCi/l or ±10 percent, whichever is larger.

References

Henry, W. M., and Loveridge, B. A., 1961, Determination of lead-210 in Harwell effluent: Atomic Energy Research Estab. Rept. R–3795, 20 p.

Rama, M. K., and Goldberg, E. D., 1961, Lead-210 in natural waters: Science, 134 p. 98–99.

Radium, dissolved, as radium-226 Precipitation method (R-1140-76)

Parameter and code: Radium, dissolved, as radium-226 (pCi/l): 09510

1. Application

The method is satisfactory for applications that do not require high precision or radium isotope identification such as routine monitoring for compliance with PCRE standards. The application is straightforward with waters of average composition, but the possibility of increased alpha self-absorption must be considered with waters of high dissolved-solids or alkaline-earth content. The internal standard technique is used when necessary.

2. Summary of method

Radium isotopes are concentrated from a water sample by coprecipitation as the sulfate with barium sulfate. The collection of radium is quantitative even though the solubility product of radium sulfate is not exceeded. Although the coprecipitation collects all radium isotopes, radium-226 is usually the predominant isotope. Results are consequently reported as concentration of radium-226. Isotopes of thorium, lead, and polonium carried down partially or completely by the barium sulfate may also contribute to the alpha count. The analytical procedure is taken from Barker and Johnson (1964).

The precipitate is collected by filtration through a plastic-membrane filter, and is counted in a low-background thin window alpha counter after a suitable delay to allow in-growth of alpha-emitting daughters. This increases the sensitivity by a factor of 4 (at equilibrium). The count rate of the sample is compared against that of a radium-226 standard carried through the procedure. Radioactive impurities in the reagents may be significant. Reagents are selected, and blanks are run with each set of samples.

Since alpha radiation is strongly absorbed by the precipitate, it is essential to keep the weight of precipitate constant in the samples, standards, and blanks. High salinity (brines), colloidal matter, and high concentrations of strontium or barium may cause problems by adding to the mass per unit area of the precipitate. Correction for increased absorption is made by use of internal standard techniques.

3. Interferences

Alpha-emitting nuclides of thorium and polonium may be carried down with the precipitate, but their concentrations are not sufficiently high in most natural water to constitute a problem.

4. Apparatus

4.1 *Beaker*, 1,500 ml.

4.2 *Filter flask*, 2,000 ml.

4.3 *Membrane filter*, 47-mm diameter, 0.45-micrometer porosity.

4.4 *Filtration assembly*, for membrane filter including funnel, sintered glass-filter support and clamp.

4.5 *Ring-and-disc sample mounts*, 47-mm diameter.

4.6 *Low-background counter*, an anticoincidence-type counter with 2-in. thin window flowing gas proportional detector preferably capable of measuring both alpha and beta activity simultaneously.

5. Reagents

5.1 *Ammonium sulfate solution* (40 percent, by weight): Dissolve 1,600 g of ammonium sulfate in a minimum volume of hot distilled water. Cool to room temperature and filter. Dilute the solution to approximately 4 liters in a 4-liter bottle.

5.2 *Barium carrier solution* (1.40 mg Ba^{+2} per ml): Dissolve 1.246 g of barium chloride dihydrate in distilled water, add 5 ml of concentrated HCl, and dilute to 500 ml.

5.3 *Hydrochloric acid,* concentrated.

5.4 *Methyl orange indicator solution.*

5.5 *Radium standard solution* I, 50.0 pCi/ml. This solution is prepared from National Bureau of Standards' encapsulated radium standard No. 4955 which contains 0.100×10^{-6} curie of radium-226 in 5 ml of 5 percent HNO_3. Rubber gloves should be worn in preparing a standard solution by the following recommended procedure.

5.5.1 Place the vial containing the radium standard in a clean, heavy-wall, small-neck bottle or flask of 250- to 500-ml capacity. Add 50 ml of 3 *N* HCl, and stopper securely with a polyethylene stopper.

5.5.2 Place the bottle (or flask) in a strong plastic sack and, holding the stopper firmly in place, shake vigorously to break the vial.

5.5.3 Decant the solution into a 2-liter volumetric flask.

5.5.4 Rinse the bottle with 50 ml of 3 *N* HCl, and decant into the 2-liter flask.

5.5.5 Add another 50 ml of 3 *N* HCl, and wash thoroughly using the ultrasonic cleaner. Decant into the 2-liter flask.

5.5.6 Rinse with 50 ml of 3 *N* HCl. Decant into the 2-liter flask.

5.5.7 Repeat steps 5.5.4 and 5.5.5 alternately, three more times each.

5.5.8 Dilute the solution in the 2-liter flask to 2,000 ml with distilled water and mix thoroughly.

The final concentrations of radium and hydrogen ion in this stock solution are: $(Ra^{+2}) = 50$ pCi/ml and $(H^+) = 0.75$ *M*.

5.6 *Radium standard solution* II, 1 ml = 10 pCi: Transfer 50 ml of the radium standard stock solution to a 250-ml volumetric flask and dilute to volume with distilled water. Add a small, clean disk or foil of 22-carat gold (surface area $\cong$ 4 cm^2) to the solution to remove polonium-210. This disk should remain in the standard solution continuously.

5.7 *Sulfuric acid wash solution:* Dilute 5 ml of concentrated H_2SO_4 to 1,000 ml with distilled water and add 3 to 4 drops of Triton X–100 surfactant (Rohm and Haas Co.).

6. Procedure

6.1 Measure 1,000 ml of the sample, previously filtered if necessary, into a 1,500-ml beaker. If the sample contains more than 350 mg/l of calcium, take a proportionately smaller volume and dilute to 1,000 ml. If a sample is believed to contain sufficient quantities of barium, strontium, or other dissolved or suspended material to add more than 1 or 2 mg to the weight of the precipitate, the internal standard modification should be used (sec. 6.8).

6.2 Prepare duplicate standard solutions, each consisting of 5.00 ml of radium standard solution (1 ml = 10 pCi radium-226) diluted to 1,000 ml with distilled water, and a blank solution consisting of 1,000 ml of distilled water. Add a few drops of methyl orange indicator, and adjust the pH to approximately 3.5 by dropwise addition of concentrated HCl (or NH_4OH followed by HCl if the sample has an initial pH below 3.5).

6.3 Heat blank solution, samples, and standard solutions to incipient boiling point, and readjust the pH to approximately 3.5.

6.4 Add 3 ml of the barium carrier solution to each beaker and stir vigorously. While stirring, add 15 ml of saturated ammonium sulfate solution. Continue heating near the boiling point for an additional 15 to 30 min.

6.5 Allow the precipitate to digest at room temperature for 4 hr or longer, then collect the precipitate on a membrane filter. Police down the beaker carefully to ensure complete transfer of the precipitate to the filter. Wash the precipitate with small volumes of the sulfuric acid wash solution. The barium sulfate precipitate should be evenly

distributed to minimize self-absorption of alpha particles. A fine jet of the wash solution can be used to redistribute the precipitate on the filter and to obtain uniform distribution.

6.6 When the membrane filter is practically dry, mount it in the ring-and-disk holders.

6.7 Determine the alpha activity of the blanks, standards, and samples after allowing the precipitates to age 15 d (or longer). Count each planchet for 100 min.

6.8 For those samples suspected of having excessive absorption loss of alpha radiation, repeat the analysis using the internal standard procedure as follows: Prepare a second sample as in 6.1. Add 5.00 ml of radium standard solution (1 ml=10 pCi). Proceed with the analytical determination as before, and count. The difference between the count rate of the sample containing the internal standard and the count rate of the sample is the basis for calculating the efficiency factor to be used.

7. Calculations

7.1 The "radium as radium-226" efficiency factor (E_a) is calculated using the following equation:

$$E_a = \frac{\bar{c}_s}{d_s},$$

where

$\bar{c}_s$ = average count rate of standard (cpm) corrected for background and blank, and

d_s = disintegration rate of standard (dpm).

7.2 The "radium as radium-226" efficiency factor (E_b), for the internal standard procedure is calculated using the following equation:

$$E_b = \frac{\bar{c}_{ss} - \bar{c}_s}{d_{ss}},$$

where

$\bar{c}_{ss}$ = average count rate (cpm) of the sample containing the internal standard, and

d_{ss} = known disintegration rate (dpm) of the internal radium standard added to the sample.

7.3 Calculation of radium gross alpha concentration, normal procedure. Use equation:

$$\text{pCi/l of Ra (as radium-226)} = \frac{1000\,\bar{c}}{KVE_a}.$$

7.4 Calculation of radium-gross alpha concentration, internal standard procedure. Use equation:

$$\text{pCi/l of Ra (as radium-226)} = \frac{1000\,\bar{c}}{KVE_b}.$$

8. Report

Report concentrations less than 1.0 pCi/l to one significant figure and concentrations above 1.0 pCi/l to two significant figures.

9. Precision

Reproducibility at the two standard deviation level is approximately ±1.0 pCi/l at concentrations of 0.5 pCi/l and below. Reproducibility is to approximately ±20 percent at higher concentrations.

Reference

Barker, F. B., and Johnson, J. O., 1964, Determination of radium in water: U.S. Geol. Survey Water-Supply Paper 1696–B, 29 p.

Radium-226, dissolved
Radon emanation method (R-1141-76)

Parameter and code: Radium-226, dissolved (pCi/l): 09511

1. Application

The method is applicable to any water sample.

2. Summary of method

The method is based on the isolation of radon-222 produced by radium-226 and measurement of the alpha activity of the radon and its short-lived daughters. The method is specific for radium-226 in contrast to the precipitation method of Barker and Johnson (1964). The procedure represents an improvement of the emanation method of Rushing (1967) in the substitution of a complexing agent to redissolve precipitated barium sulfate. Formerly a complex procedure for resolution involving a strong acid, ashing, and evaporation was required. Radon is measured in a modification of the alpha scintillation cell of Lucas (1957).

Dissolved radium in filtered water is collected by coprecipitation with barium sulfate. The precipitate is centrifuged and then dissolved in alkaline sodium diethylene triamine pentacetate solution. The solution is transferred to a radon bubbler, and any radon present is removed by purging with helium gas. Fresh radon is then allowed to grow in. After several days the ingrown radon is purged into an alpha scintillation cell, short-lived daughters are allowed to grow in, and the alpha-count rate is then determined. The radium-226 concentration in the original water sample is calculated from the radon determination on the basis of the rate of radon production with time.

3. Interferences

The method is normally specific for radium-226. Radium-223 and radium-224 produce radon-219 and radon-220, respectively. Neither of these interfere directly, but the 10.6 hr lead-212 from radon-220 has alpha-emitting daughters which could interfere. A wait of 2 or 3 d before counting eliminates the interference. The alpha-emitting daughters of radon-219 have no effect if sufficient waiting time is allowed for complete decay of the 36 min lead-211.

4. Apparatus

4.1 *Alpha-counting apparatus*, scaler and high voltage power supply, preamp and amplifier with discriminator.

4.2 *Beaker*, 1,500 ml.

4.3 *Gas delivery system*, for helium gas.

4.4 *Mixer*, wiggle-plate or ultrasonic type.

4.5 *Radon deemanation train and bubbler* (fig. 5).

4.6 *Radon scintillation cell and housing* (fig. 6).

5. Reagents

5.1 *Barium carrier solution*, 50 mg barium/ml: Dissolve 75.81 g barium chloride ($BaCl_2$) in distilled water and dilute to 1,000 ml.

5.2 *Defoaming emulsion*, Dow Corning Anti Foam H-10 emulsion, or equivalent: Dilute to approximately 4 to 5 percent solution with distilled water before using.

5.3 *DPTA-TEA solution:* Dissolve 10 g of sodium hydroxide pellets in a beaker containing 60 ml of distilled water, and stir in

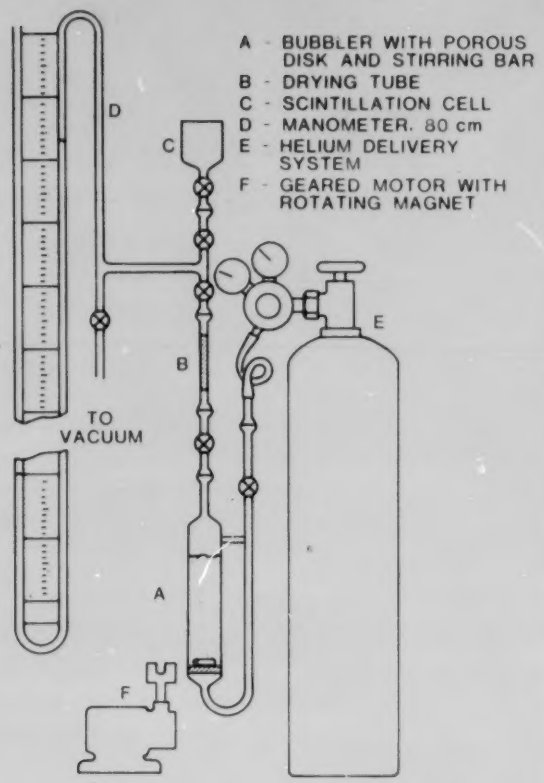


Figure 5.—Radon deemanation train and bubbler.

cold-water bath until dissolved. Add 20 g of purified diethylene triamine penta acetic acid (DPTA), and continue stirring until dissolved. Add 17 ml of 50-percent triethanolamine, mix and dilute to 100 ml. Store in Teflon bottle.

5.4 *Radium standard solution* I, 1 ml = 50.0 pCi: This solution is prepared from National Bureau of Standards' encapsulated radium standard No. 4955 which contains 0.100×10^{-6} curie of radium-226 in 5 ml of 5 percent HNO_3. Rubber gloves should be worn in preparing a standard solution by the following recommended procedure.

5.4.1 Place the vial containing the radium standard in a clean, heavy-wall, small-neck bottle or flask of 250- to 500-ml capacity. Add 50 ml of 3 *N* HCl and stopper securely with a polyethylene stopper.

5.4.2 Place the bottle (or flask) in a durable plastic sack, and, holding the stopper firmly in place, shake vigorously to break the vial.

5.4.3 Decant the solution into a 2-liter volumetric flask.

5.4.4 Rinse the bottle with 50 ml of 3 *N* HCl and decant into the 2-liter flask.

5.4.5 Add another 50 ml of 3 *N* HCl and wash thoroughly using the ultrasonic cleaner. Decant into the 2-liter flask.

5.4.6 Rinse with 50 ml of 3 *N* HCl. Decant into the 2-liter flask.

5.4.7 Repeat steps 5.4.4 and 5.4.5 alternately, three more times each.

5.4.8 Dilute the solution in the 2-liter flask to 2 liters with distilled water and mix thoroughly.

The final concentrations of radium and hydrogen ion in the stock solutions are: $(Ra^{+2}) = 50$ pCi/ml and $(H^+) = 0.75$ mole/l.

5.5 *Radium standard solution* II, 1 ml = 1.000 pCi: Dilute 10.00 ml radium standard solution I and 10 ml of concentrated HCl to 500 ml with distilled water.

5.6 *Sulfuric acid wash solution:* Add 5 ml of concentrated H_2SO_4 and 3–5 drops of Triton X–100 to 4 liters of distilled water.

5.7 *Sulfuric acid*, concentrated.

6. Procedure

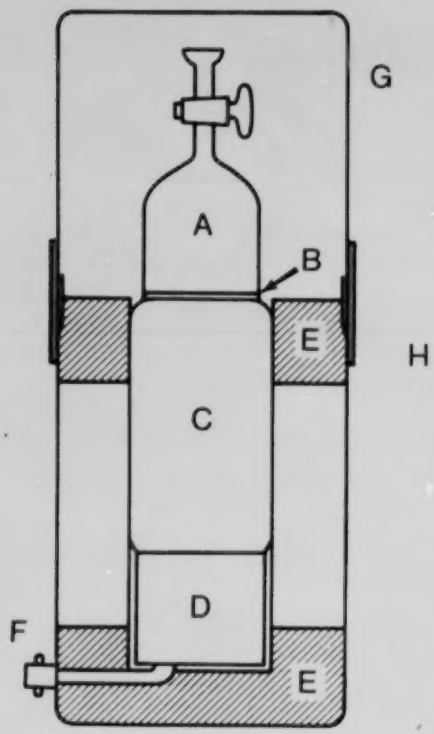
6.1 Coprecipitation of radium with barium sulfate.

6.1.1 Add 5 ml concentrated hydrochloric acid to 1,000 ml of filtered water sample contained in a 1,500-ml beaker.

6.1.2 Add 1 ml of 50 mg/ml barium carrier to the sample and stir.

6.1.3 Cautiously add 20 ml of concentrated sulfuric acid to each sample with constant stirring. (Use of a 500-ml dispensing flask fitted with a 50-ml delivery head facilitates the acid addition.) Stir well after the acid addition. Allow barium sulfate precipitate to settle overnight.

6.1.4 Carefully remove the supernate by decantation or suction, and quantitatively transfer the balance of the supernate and precipitate to a 40-ml centrifuge tube using a rubber policeman and small quantities of dilute sulfuric acid-Triton-X–100 wash solution.



A - SCINTILLATOR CELL - KOVAR BELL COATED INSIDE WITH ACTIVATED PHOSPHOR

B - QUARTZ WINDOW CEMENTED TO SCINTILLATOR BELL

C - PHOTOMULTIPLIER TUBE

D - TUBE BASE WITH VOLTAGE DIVIDER

E - POLYURETHANE CENTERING RING AND SUPPORT

F - HIGH VOLTAGE AND SIGNAL CONNECTION

G - LIGHT-TIGHT METAL HOUSING

H - ELASTIC LIGHT TIGHT FELT SURROUND

Figure 6.—Radon scintillation cell and housing.

6.1.5 Centrifuge as necessary, decant, and discard supernate.

6.1.6 Add approximately 10 ml of distilled water and 1.5 ml of DTPA reagent to the precipitate in the centrifuge tube. Disperse the precipitate in each tube by using a wiggle-plate mixer or an ultrasonic unit. Place tubes in a wire rack, and immerse rack and tubes to a depth of approximately 1 inch in a boiling-water bath.

6.1.7 Complete dissolution should occur within a few minutes if the barium sulfate "pellet" was adequately dispersed. Occasionally, volume of solution in the centrifuge tubes may decrease by 4–5 ml as a result of prolonged heating, and the precipitate may not dissolve. Addition of distilled water to bring the volume to approximately 20 ml maximum plus additional redispersion and heating will usually result in rapid dissolution of even difficulty soluble precipitates. After the precipitate has dissolved, cool the tubes.

6.2 Deemanations.

6.2.1 Using a funnel with a fine tip, transfer the cooled solution to a clean bubbler. Wash the centrifuge tube several times with distilled water, and add the washings and sufficient additional water to the bubbler to leave approximately 2 cm of airspace at the top. Add 1–3 drops of 4 percent silicone defoaming emulsion to the solution in the bubbler to minimize frothing during purging.

6.2.2 Attach stopcock and "O" ring to bubbler using clamp, leaving outlet stopcock on bubbler assembly in open position. Attach helium line (3–5 psi) to inlet side of bubbler. Slowly open stopcock on inlet until a stream of fine bubbles rises from the porous disk. Maintain a steady flow of bubbles through the sample for approximately 20 min to completely purge all ingrown radon from the solution. Close inlet stopcock and allow pressure under porous disk to equalize momentarily. Close outlet and record the day, hour, and minute. This is zero time for the growth

of radon that will be removed in the second deemanation and counted.

6.2.3 Allow from 2 to 20 d in-growth time for radon-222 depending upon the radium-226 concentration in the original sample, volume of sample used, and so forth.

6.2.4 The second deemanation is made by setting up the bubbler as in 6.2.2 except that both stopcocks are initially closed. Attach bubbler to drying tube with "O" ring and clamp. Evacuate purging assembly, including cell, with vacuum pump for approximately 1.5 to 2 min. Close stopcock at vacuum pump, turn pump off, and momentarily crack vacuum-pump connection. Open stopcock in helium line above bubbler-inlet stopcock and momentarily crack "O" ring connection to purge trapped air from line and bubbler-inlet connection. Clamp and allow system to stand for approximately 2 min. If system leaks, manometer meniscus will flatten or manometer will begin to fall. If meniscus remains stable, proceed to next step.

6.2.5 Carefully open bubbler-outlet stopcock until manometer begins to fall (check porous disk for fine bubbles). Allow vacuum to equilibrate slowly (otherwise there is excessive risk of drawing liquid sample into drying tube). Bubbling will slow appreciably in a few seconds. Slowly open outlet stopcock complete. Then continue with purging by slowly opening bubbler-inlet stopcock, checking porous disk carefully for rising bubbles. (*Flow rate must be closely controlled again at this point, to prevent sudden surge of liquid into drying tube.*) Allow pressure to build up slowly, controlling manometer fall rate to complete purging in 15–20 min. To prevent cell leakage during counting, close the cell stopcock at approximately 4 mm below atmospheric pressure.

6.2.6 Close down purging assembly stopcocks from cell to helium inlet in sequence as rapidly as possible. *Record time.* Remove bubbler from assembly quickly, and crack outlet stopcock momentarily to release helium pressure.

6.2.7 Place cell in light-tight counting chamber. Allow to age 3 or 4 hr before counting. Count overnight (1,000 min) for the average water sample.

6.2.8 Dates, times, counts, and all other pertinent sample information should be recorded on data and calculation sheets.

6.3 Calibration of equipment: One low (≅10 cpm) and one high (≅1,000 cpm) count rate disk standards are useful for routine instrument calibration tests and for determining photomultiplier tube plateau curves. Prepare by precipitating each of two standards containing 5 and 500 pCi of radium-226 with 50 mg of barium sulfate respectively as previously described. Mount the precipitate by filtering through a 47-mm 0.45-micrometer membrane filter. Dry and place on the disc of a ring-and-disc assembly. After drying, cover the precipitate on the filter with a Mylar disk coated with an alpha-sensitive phosphor. The dull phosphor-coated side should be placed against the sample. Cover with the ring, press into place, and then seal the assembly with several pieces of cellophane tape to prevent it from separating.

The high count rate standard is used to determine the plateaus for each photomultiplier tube, and the appropriate operating voltage is then chosen accordingly. The low count rate standard is used to check instrument operating conditions at low count rates comparable to those of typical samples.

Frequently operating characteristics of two or more photomultiplier-counting systems are sufficiently similar to enable the use of a single high-voltage power supply.

Minor differences in the counting efficiency of each unit can be adjusted by the use of a focusing potentiometer on each photomultiplier housing.

Long-term instrument backgrounds should be obtained for each counting system and should not generally exceed 0.005 cpm.

Scintillation cell background count rates should be determined periodically for each cell in combination with each instrument. Generally, background count rates are determined using a minimum of 1,000 min. Background count rates for a specific cell may vary considerably from one instrument to an-

other, but should not generally exceed 0.10 to 0.15 cpm.

After long use or after counting a high-radium-content sample, background rates in some scintillation cells may become excessive (>0.15 cpm) for low-level work. In that event the cells must be used only for relatively high-level samples. Original low background may be restored by rebuilding.

6.4 Experimental determination of counting efficiency: The counting efficiency of each scintillation cell varies between cells and between counting instruments. Consequently, for the most accurate work, the counting efficiency of each scintillation cell should be determined in each instrument in which it is used.

The counting efficiency for each cell-instrument unit is determined by counting radon transferred from a "standard bubbler" containing a measured amount of radium-226 standard solution. A minimum of four or five standards or one for each counting instrument enables four or five cells to be calibrated simultaneously. Waiting time for radon in-growth is also considerably reduced as compared to that required if only one standard is available.

Standards are prepared by pipetting 10.0 ml of 10-pCi/ml radium-226 standard solution directly into each of several bubbler tubes. The tubes are fitted with an "O" ring stopcock assembly, and then deemanated to determine the zero in-growth time for radon in the same manner as a sample. Barring any spillage or breakage, the standards will last indefinitely and can be deemanated every 4 or 5 d to provide radon for calibration purposes.

Cell-counting efficiencies are generally about 5.3 cpm/pCi of radon-222 after in-growth of daughters for 3 hr, but this may vary considerably depending upon factors including the age of the cell, phototube condition, and moisture in cells. Erratic results are sometimes obtained as a result of improper cell or instrument grounding, loose connections, noisy power lines, and so forth.

7. Calculations

7.1 Radon counting efficiency factors (E). The calculation requires corrections for radon in-growth and radon decay. The radon in-growth and decay curves and their relation to the time intervals that appear in the equation are shown in figure 1. Substitute the experimental data obtained for each cell-instrument unit (sec. 6.4) into a modified form of equation 4.

$$E = \frac{\bar{c}_n}{d_n(1-e^{-\lambda_1 t_1})\,(e^{-\lambda_1 t_4})},$$

where

λ_1 = decay constant of radon-222 (1.259×10^{-4} min^{-1}),

t_1 = time interval for buildup of radon between the previous deemanation of the standard (point A, fig. 1) and the present deemanation (point B),

t_4 = time interval between deemanation standard (point B) and midpoint of the counting time, $= t_2 + \frac{t_3}{2}$,

where

t_2 = time interval between deemanation of the standard, (point B) and the beginning of the count time (point C),

t_3 = half the time interval between the beginning (point C) and the end (point D) of the counting time, and

$\bar{c}_n$ and d_n are as defined in equation 2.

7.2 Calculation of radium-226 concentration: Efficiency (E) used for an individual sample is that determined for the cell and instrument used to count the sample. An in-growth factor is introduced because of in-growth of radon with time after the first deemanation. Use a modified form of equation 3 when counting time is less than 3,600 minutes.

pCi/l of radium-226

$$= \frac{1000\,\bar{c}}{KVE(1-e^{-\lambda_1 t_1})\,(e^{-\lambda_1 t_4})},$$

where

t_1 = time interval for in-growth of radon betwen first deemanation (step 6.2.1) and second deemanation (step 6.2.5) of the sample, and

t_4 = time interval between second deemanation of the sample (step 6.2.5) and midpoint of the sample counting time, $= t_2 + \frac{t_3}{2}$.

The other symbols are as defined in section 7.1.

When counting time exceeds 3,600 minutes, use equation 3 including the term for correction for decay during the count.

pCi/l of radium-226

$$= \frac{1000\,\bar{c}_1 t_3}{KVE(1-e^{-\lambda_1 t_1})\,(e^{-\lambda_1 t_2})\,(1-e^{\lambda_1 t_3})},$$

where

t_2 = delay before counting, point B to C, figure 1, and

t_3 = time interval of count, point C to D.

The other symbols are as defined in 7.1 and 7.2.

Radon decay and in-growth factors are easily and accurately calculated with an electronic calculator having natural log and e^x functions. The table of "Radon fraction ($e^{-\lambda t}$) remaining after radioactive decay for specified times," for commonly used time intervals (table 1) may also be used.

8. Report

Report concentrations less than 0.10 pCi/l to one significant figure and values above 0.10 pCi/l to two significant figures.

Table 1.—Radon fraction ($e^{-\lambda t}$) remaining after radioactive decay for specified times

[Radon $T^{1/2}$ = 3.823 d]

Time	Days	Hours	Minutes	Time	Minutes
1	0.834,18	0.992,47	0.999,87	31	0.996,10
2	.695,85	.985,00	.999,75	32	.995,98
3	.580,46	.977,59	.999,62	33	.995,85
4	.484,21	.970,23	.999,50	34	.995,73
5	.403,91	.962,93	.999,37	35	.995,60
6	.336,93	.955,68	.999,24	36	.995,48
7	.281,07	.948,49	.999,12	37	.995,35
8	.234,46	.941,35	.998,99	38	.995,23
9	.195,58	.934,27	.998,87	39	.995,10
10	.163,15	.927,24	.998,74	40	.994,98
11	.136,09	.920,26	.998,62	41	.994,85
12	.113,53	.913,33	.998,49	42	.994,73
13	.094,70	.906,46	.998,36	43	.994,60
14	.079,00	.899,64	.998,24	44	.994,48
15	.065,90	.892,87	.998,11	45	.994,35
16	.054,97	.886,15	.997,99	46	.994,22
17	.045,86	.879,48	.997,86	47	.994,10
18	.038,25	.872,86	.997,74	48	.993,97
19	.031,91	.866,29	.997,61	49	.993,85
20	.026,62	.859,77	.997,48	50	.993,72
21	.022,20	.853,30	.997,36	51	.993,60
22	.018,52	.846,88	.997,23	52	.993,47
23	.015,45	.840,50	.997,11	53	.993,35
24	.012,89	.834,18	.996,98	54	.993,22
25	.010,75	------	.996,86	55	.993,10
26	.008,97	------	.996,73	56	.992,97
27	.007,48	------	.996,61	57	.992,85
28	.006,24	------	.996,48	58	.992,72
29	.005,21	------	.996,36	59	.992,60
30	.004,34	------	.996,23	60	.992,47

9. Precision

On the basis of limited data the precision at the 0.10 pCi/l level is estimated at ±20 percent Above 0.10 pCi/l the precision is estimated at ±10 percent

References

Barker, F. B., and Johnson, J. O., 1964, Determination of radium in water: U.S. Geol. Survey Water-Supply Paper 1696–B, 29 p.

Lucas, H. F., 1957, Improved low-level alpha scintillation counter for radon: Rev. Sci. Instr., no. 28, 680–683.

Rushing, D. E., 1967, Determination of dissolved radium in water: Am. Water Works Assoc. Jour. no. 59, 593–600.

Do Not Film This Page

Radium-228, dissolved
Determination by separation and counting of actinium-228 (R-1142-76)

Parameter and code: Radium-228, dissolved (pCi/l): none assigned

1. Application

The method is applicable to all natural-water samples. Applications to samples containing reactor effluent or other contaminants have not been evaluated.

2. Summary of method

The method is based on the chemical separation and subsequent beta counting of actinium-228, the daughter of radium-228. Radium-228 is not determined directly because of the difficulty of counting its weak beta emission in the presence of other alpha-emitting radium isotopes and their beta-emitting daughters (Johnson, 1971).

3. Interferences

No chemical interferences have been detected. Because of chemical similarity, radionuclides of the actinide elements and the rare-earth elements may accompany the actinium precipitate. Significant concentrations of these would be expected only in areas where nuclear fission or nuclear research is carried on.

Radiochemical interferences are unlikely to occur in natural waters. Decontamination factors for other natural radionuclides appear to be 5,000 or greater. Exhaustive tests for artificially produced radionuclides have not been made, but little or no interference has been detected for cesium-137, strontium-90, and yttrium-90. Lanthanum-140 appears to be the most probable interference, but this and other rare-earth nuclides would be encountered only in waters contaminated by reactor effluent.

Success of the method at low levels of radioactivity depends largely upon use of reagents essentially free of radioactive contamination. Purity of the yttrium reagent is especially important.

4. Apparatus

4.1 *Centrifuge.*

4.2 *Centrifuge tubes,* 40- or 50-ml capacity, heavy-walled.

4.3 *Drying lamp,* infrared, mounted in ringstand.

4.4 *Hotplate.*

4.5 *Low-background counter,* an anticoincidence-type counter with 2-in. thin window flowing gas proportional detector preferably capable of measuring both alpha and beta activity simultaneously.

4.6 *Planchets,* 50-mm diameter, concentric-ring type.

4.7 *Stirring rods,* Teflon.

5. Reagents

5.1 *Ammonium hydroxide,* concentrated.

5.2 *Ammonium sulfate solution,* 200 mg/ml: Dissolve 200 g of ammonium sulfate in distilled water and dilute to 1 liter.

5.3 *Ammonium sulfide solution,* 2 percent: Dilute 10 ml of 20–23 percent aqueous ammonium sulfide solution to 100 ml.

5.4 *Barium carrier solution,* 1 ml = 16.00 mg Ba^{+2}: Dissolve 28.46 g of $BaCl_2 \cdot 2H_2O$ in distilled water, add 2 ml of concentrated nitric acid, and dilute to 1,000 ml.

5.5 *Binder solution:* Dissolve about 1 g of "Duco" cement in 100 ml acetone.

5.6 *Citric Acid, 1 M:* Dissolve 210.1 g of citric acid monohydrate in distilled water and dilute to 1,000 ml.

5.7 *EDTA* reagent, 0.25 *M* EDTA containing 20 mg/ml NaOH: Dissolve 20 g of NaOH in about 750 ml distilled water. Heat, and slowly add 93 g of disodium ethylenediaminetetraacetate while stirring. When dissolution is complete, cool, and dilute to 1,000 ml.

5.8 *Lead carrier solution* I, 1 ml = 15.00 mg Pb^{+2}: Dissolve 23.97 g of $Pb(NO_3)_2$ in distilled water; add 2 ml of concentrated nitric acid, and dilute to 1,000 ml.

5.9 *Lead carrier solution* II, 1 ml = 1.50 mg Pb^{+2}: Dilute 100 ml of lead carrier solution I to 1,000 ml.

5.10 *Methyl orange indicator solution.*

5.11 *Nitric acid,* concentrated.

5.12 *Sodium hydroxide, 10 N:* Dissolve 400 g of NaOH pellets in distilled water and dilute to 1 liter. Store in a polyethylene or Teflon bottle.

5.13 *Sulfuric acid, 18 N:* Cautiously add 500 ml concentrated H_2SO_4 while stirring into about 400 ml distilled water; cool, and dilute to 1,000 ml.

5.14 *Radium-228 standard:* The preparation of the standard solution is complicated by the fact that a standard of radium-228 is not readily obtainable. Generally the radium-228 must be obtained from thorium metal or pure compounds sufficiently old to permit equilibrium in-growth of radium-228. In 40-year-old material the radium-228 daughter has reached 99 percent of equilibrium concentration. The following procedure is used to accurately prepare standardized thorium-232 and radium-228 from thorium oxide approximately 50 yr old.

5.14.1 Weigh out a 1.0000 g sample of thorium dioxide.

5.14.2 Transfer the sample to a 250-ml Erlenmeyer flask containing 20 ml of acid mixture (15.7 *N* HNO_3, 0.05 *N* HF). Carefully heat and stir the mixture until the ThO_2 dissolves. Transfer the solution to a 200-ml volumetric flask and add a little barium nitrate solution containing 5–15 μg of barium. Make up to volume with 1 *N* nitric acid. Activity of radium-228 in the solution is calculated as follows:

$$\text{Radium-228 (dpm/ml)} = 246W\,(1-e^{0.1205t}),$$

where

W = thorium concentration in mg/ml, and

t = years since thorium dioxide was prepared.

At equilibrium 1 mg thorium = 246 dpm radium-228.

5.15 *Yttrium carrier solution,* 1 ml = 18 mg Y^{+3}: Add 22.85 g of Y_2O_3 to a 250-ml Erlenmeyer flask containing 20 ml of water. Swirl, place on a hotplate, and heat to boiling. Slowly and cautiously add concentrated nitric acid, while stirring, until a homogeneous solution is obtained. (Usually about 30 ml of nitric acid is required. It is sometimes necessary to add more water.) Add an additional 70 ml of concentrated nitric acid and dilute to 1 liter. Note: The yttrium oxide must be as free as possible of beta activity (usually due to isotopes of actinium). Yttrium oxide suitable for carrier preparation has been obtained from American Potash and Chemical Corp., West Chicago, Ill.

5.16 *Yttrium-strontium carrier solution,* 1 ml = 0.9 mg Sr^{+2} and 0.9 mg Y^{+3}: Dissolve 434.8 mg of $Sr(NO_3)_2$ in distilled water; add 10 ml of yttrium carrier solution, and dilute to 200 ml.

6. Procedure

6.1 Use 1–4 liters of sample, on the basis of the expected radium-228 content, and evaporate to 1 liter, if necessary. Add 5 ml of citric acid for each liter of original sample, and then add a few drops of methyl orange indicator. If the solution is yellow, add nitric acid until the red color is obtained.

Prepare standards by dilution of appropriate volumes of the "old" thorium-radium solution to 1 liter. A disintegration rate of approximately 1,000 dpm is appropriate. Carry the standards through the procedure in the same way as a sample.

6.2 Add 10 ml of lead carrier solution I, 2 ml of barium carrier solution, and 1 ml of yttrium carrier solution. Heat to incipient boiling, and maintain at this temperature for about 30 min with frequent stirring.

6.3 Add concentrated ammonium hydroxide until the yellow color of methyl orange is obtained; then add a few drops excess. Precipitate lead and barium sulfates by adding 18 *N* sulfuric acid until the red color reappears; then add 0.25 ml excess. Add 15 ml of ammonium sulfate solution for each liter of solution; keep the sample at a temperature of about 90°C for 30 min and stir frequently. Remove from the hotplate and allow to settle for at least 2 hr; then siphon or decant most of the supernatant liquid and discard.

6.4 Transfer the precipitate to a 40-ml centrifuge tube; centrifuge, and discard the supernatant liquid.

6.5 Wash the precipitate twice with concentrated nitric acid using centrifugation wash techniques. Add 25 ml of EDTA reagent. Heat in a hot-water bath and stir intermittently, adding a little additional 10 *N* NaOH if the precipitate does not dissolve readily.

6.6 Add 1 ml of strontium-yttrium carrier solution. Stir thoroughly; add a few drops of 10 *N* NaOH if any precipitate forms.

6.7 Add 1 ml of ammonium sulfate solution and stir thoroughly; then add glacial acetic acid dropwise until barium sulfate precipitates, and add 2 ml excess. Allow the precipitate to digest in a hot-water bath until the precipitate has largely settled. Centrifuge, then discard the supernatant liquid.

6.8 Add 20 ml of EDTA reagent, heat, and stir until the barium sulfate precipitate dissolves. Repeat steps 6.6 and 6.7.

6.9 Dissolve the barium sulfate precipitate in 20 ml of EDTA reagent, and add 1 ml of yttrium carrier solution and 1 ml of lead carrier solution. If any precipitate forms it should be dissolved by adding a few drops of 10 *N* NaOH. Transfer the solution to a Teflon or polyethylene container. Record the date and time. Age for 36 hr or longer. Cover the sample to prevent evaporation.

6.10 Transfer the aged solution to a centrifuge tube, and add 0.3 ml of ammonium sulfide solution. Add 10 *N* NaOH dropwise while stirring vigorously, until lead sulfide precipitates; then add about 10 drops excess. Stir intermittently over a period of about 10 min. The lead sulfide should settle as a fine-granular precipitate.

6.11 Centrifuge the solution, and transfer the supernatant liquid to clean centrifuge tubes. Discard the residue.

6.12 Place the centrifuge tube in a hot-water bath and slowly add 10 *N* NaOH to the liquid while stirring, until yttrium hydroxide precipitates; add 1 ml excess and stir intermittently for several minutes. Record the date and time of the precipitation. Centrifuge as soon as the yttrium hydroxide has largely settled. Discard the supernate.

6.13 Wash the precipitate thoroughly with 5 ml of water containing about 10 drops of 10 *N* NaOH, centrifuge, and discard the wash solution.

6.14 Transfer the precipitate to a 5-cm counting planchet, using small volumes of distilled water, while drying under an infrared light lamp. The last washing should contain 1 ml of binder solution.

6.15 Count the sample in a low-background beta counter for a sufficient length of time to obtain satisfactory counting statistics. Record date and time that count begins. For most natural waters a counting period of about 300 to 500 min is desirable because of the low concentration of radium-228.

7. Calculations

7.1 Radium-228 (actinium-228) efficiency factor: The calculation requires a factor for in-growth of the actinium daughter and for decay in the time interval between separation from the radium parent and beginning of count.

The chemical recovery factor is included in overall efficiency and is not separately identified. Use equation 4 omitting the f_n term.

$$E = \frac{\overline{c_n}}{d_n (e^{-\lambda t_n}) (1 - e^{-\lambda_1 t_1}) (e^{-\lambda_1 t_3})},$$

where

λ = decay constant of radium-228 (0.1205 yr^{-1}),

λ_1 = decay constant of actinium-228 (0.001885 min^{-1}),

t_s = elapsed time between certification of the standard and time of count in years,

t_1 = time interval between final purification of barium-radium sulfate precipitate (step 6.9) and separation of actinium daughter (aging time in minutes) (step 6.12), and

t_2 = time interval between separation of actinium daughter (step 6.12) and counting in minutes.

7.2 Calculation of radium-228 concentration: Use equation 3 omitting the f term. Correction for decay of radium-228 is seldom required. In addition to in-growth and decay times for actinium-228 cited under 7.1 a correction for decay during counting is required.

$$\text{pCi/l of radium-228} = \frac{1{,}000c\ \lambda_1 t_3}{KVE\,(e^{-\lambda t_s})\,(1-e^{-\lambda_1 t_1})\,(e^{-\lambda_1 t_2})\,(1-e^{-\lambda t_3})},$$

where

t_s = decay time of radium-228 between sampling and analysis in years, and

t_3 = counting time in minutes.

The other symbols are defined in section 7.1.

8. Report

Report values of less than 1.0 pCi/l to one significant figure and values above 1.0 pCi/l to two significant figures.

9. Precision

The limited data available suggest that precision of the method is approximately ±20 percent for a concentration of 1 pCi/l and ±10 percent at the 10 pCi/l level or above.

Reference

Johnson, J. O., 1971, Determination of radium-228 in natural water: U.S. Geol. Survey Water-Supply Paper 1696–G, 26 p.

Radioruthenium, dissolved, as ruthenium-106 Distillation method (R-1150-76)

Parameter and code: Radioruthenium as ruthenium-106, dissolved (pCi/l): none assigned

1. Application

This method is applicable to analysis of nonsaline waters which do not contain high concentrations of organic matter. Using a maximum sample volume of 100 ml, the detection limit is approximately 4 pCi/l. Because of this rather high detection limit, the method is of value primarily for water samples which have substantial fission product activity. The sensitivity may be improved by preconcentrating the ruthenium and by counting the sample more than the recommended 150 min.

2. Summary of method

Ruthenium salts form the tetroxide in acid solution when a strong oxidizing agent is present. This oxide melts near room temperature and can be easily volatilized from concentrated perchloric acid solution, which boils at approximately 200°C. Distillation of the tetroxide provides an excellent separation from almost all potential sources of interference.

The method used is essentially that described by Glendenin (1951). The water sample is evaporated to small volume, and stable ruthenium carrier is added. Nitric acid is added to oxidize organic matter, phosphoric acid is added to prevent volatilization of molybdenum, bromide and iodide are added as halogen holdback carriers, and sodium bismuthate is added to oxidize the halide ions to their respective nonvolatile oxyacids (Wyatt and Rickard, 1961). Finally, perchloric acid is added to oxidize ruthenium to the tetroxide and to provide a high boiling point for the solution. Ruthenium tetroxide is then distilled, with the aid of air bubbles through the solution, into a cold sodium hydroxide solution. Ethyl alcohol is added to precipitate the ruthenium as mixed oxides.

The ruthenium oxides are separated from the supernate by centrifugation, redissolved in hydrochloric acid, and then reduced to ruthenium metal-oxide mixture by addition of magnesium turnings. After dissolving the excess magnesium, ruthenium is recovered by filtration through a tared filter and counted on a low-background beta counter. Recovery is determined gravimetrically. The corrected activity is compared with that of standards similarly prepared to determine the ruthenium-106 activity of the sample.

The restriction of the method to freshwaters and low-sample volumes is necessary to avoid large amounts of solids in the distillation flask. The range of usable sample volumes as a function of dissolved solids has not be evaluated.

3. Interferences

Because the analytical method separates pure ruthenium, only ruthenium isotopes can interfere. On the basis of half-life, ruthenium-103 is the only interference of practical significance. The ruthenium-103 contribution to the total count is less than ruthenium-106 contribution (for equal numbers of atoms) because of lower counting efficiency. The ruthenium-103 contribution

decreases with time and may be completely eliminated by several months decay. Alternatively, the relatively low-energy betas from ruthenium-103 may be eliminated by counting the sample through an absorber which does not significantly affect the higher energy betas from rhodium-106 (ruthenium-106).

Any organic matter present in the sample should be destroyed by boiling with a concentrated nitric-perchloric acid mixture before proceeding with the perchloric acid distillation. To prevent explosive decomposition of the distillation mixture, nitric acid should be present as long as any unoxidized organic material remains.

Large amounts of insoluble matter in the distillation flask may cause serious bumping and impair the recovery of ruthenium.

4. Apparatus

4.1 *Compressed air*, 1–2 psi supply for bubbling air through distillation flask.

4.2 *Low-background counter*, an anti-coincidence-type counter with 2 in. thin window flowing gas proportional detector preferably capable of measuring both alpha and beta activity simultaneously.

4.3 *Burner*, Bunsen, small.

4.4 *Centrifuge*, capable of accepting 40-ml tubes.

4.5 *Centrifuge tubes*, 40-ml, heavy-wall.

4.6 *Distillation apparatus*. See figure 7.

4.7 *Filter disks*, Versapore, 47 mm, 5 micrometer (Gelman Instrument Co., Ann Arbor, Mich. 48106).

4.8 *Hotplate*.

4.9 *Vacuum desiccator*.

4.10 *Vacuum-filtration apparatus* for 47-mm filters.

5. Reagents

5.1 *Bromide-iodide solution*, 1 ml = 10 mg Br and 10 mg I: Dissolve 4.7 g NaI and 5.2 g NaBr in 400 ml distilled water.

5.2 *Diethyl ether*.

5.3 *Ethanol*, 95 percent.

5.4 *Hydrochloric acid*, concentrated and 6 *M*.

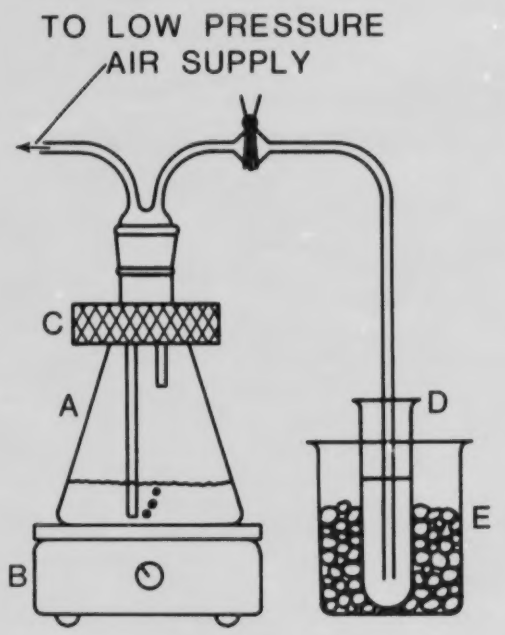


Figure 7.—Apparatus for distillation of ruthenium tetroxide.

5.5 *Magnesium metal* turnings.

5.6 *Nitric acid*, concentrated.

5.7. *Perchloric acid*, 70 percent.

5.8 *Phosphoric acid*, concentrated (85 percent).

5.9 *Ruthenium carrier solution:* Suspend 5 g of purified $RuCl_3$ in approximately 250 ml of 6 *M* HCl and agitate for several hours or overnight on a mechanical shaker. Filter the resulting solution through a fine filter. The solution is standardized by direct reduction of aliquots with magnesium metal, followed by filtration and weighing of the

mixed ruthenium oxide and metal produced. Care should be exercised to dissolve excess magnesium with HCl and to thoroughly wash the precipitate before drying.

5.10 *Ruthenium standard:* Prepare standard deposits of ruthenium-106 on filter paper starting with ruthenium standard solution of 100 pCi in 5 ml. Follow steps 6.12 through 6.16 in the "Procedure" section. Correct the activity determined for decay.

5.11 *Sodium bismuthate.*

5.12 *Sodium hydroxide, 6 M.*

6. Procedure

6.1 Estimate the volume of sample on the basis of dissolved solids. The volume is selected to avoid excess precipitation of salts in the evaporation step. The distillation flask holds 50 ml without danger of losing sample. Sample volumes in excess of this are evaporated to 50 ml in a Teflon evaporating dish.

6.2 Transfer the water sample into the distillation flask, and evaporate down to approximately 5 ml. Add an accurately measured amount of ruthenium carrier between 20 and 30 mg. Record pipet volume to 0.01 ml.

6.3 Evaporate to less than 5 ml. (Precipitation will usually occur, but the residue must not go dry.) Cool the flask and contents.

6.4 Add the following reagents in order: 1 ml concentrated nitric acid, 1 ml concentrated phosphoric acid, 2 ml bromide-iodide reagent, 0.5 g sodium bismuthate, and 10 ml 70 percent perchloric acid. Mix thoroughly.

6.5 Place the lead-ring weight around the flask. Moisten the ground-glass joint with phosphoric acid, and attach the delivery apparatus to the flask. Place the distillation apparatus on a hotplate, and immerse the end of the delivery tube in a 40-ml centrifuge tube containing 12 ml of 6 *M* NaOH. The centrifuge tube is kept immersed in an ice bath.

6.6 Connect the air supply to the still, and adjust the flow rate to a few bubbles per second. Heat the flask slowly to the boiling point, and then heat strongly to distill the ruthenium. Note: It is best to perform the distillation behind an explosion shield.

6.7 Continue the distillation until the dense white fumes of perchloric acid have been carried over for a few minutes. Total time required for the distillation is usually 20–30 min.

6.8 Lower the centrifuge tube from the delivery tube, and remove the still from the hotplate. Disconnect the air supply and allow the still to cool. When cool, rinse the contents of the delivery tube into the centrifuge tube with a little distilled water from a washbottle.

6.9 Carefully warm the centrifuge tube to near boiling over a small burner. Remove from the flame and add, in small amounts, 3 ml of 95 percent ethanol, reheating to incipient boiling after each small addition. It is important to swirl the solution constantly while heating.

6.10 Cool the solution, and centrifuge to recover the precipitated ruthenium oxides. The supernate should be colorless and may be discarded.

6.11 Suspend the precipitate in 10 ml of distilled water to which 1 ml of 6 *M* NaOH has been added. Heat (with swirling) to boiling. Centrifuge and discard the supernate.

6.12 Suspend the precipitate in a few milliliters of 6 *M* HCl and reheat to boiling (swirl vigorously). Continue heating for a few minutes to dissolve all solid material. Set aside to cool.

6.13 Add about 5 ml distilled water to the ruthenium solution; then add small portions of magnesium turnings to reduce the ruthenium to the mixed oxide-metal precipitate. The solution may have to be heated to boiling as the reaction nears completion (supernate has light-blue color) to speed the process.

6.14 Add (slowly, at first) about 5 ml of concentrated HCl, and then heat to boiling for a few minutes to dissolve any excess magnesium.

6.15 Filter the suspension through a tared 47-mm Versapore filter using a vacuum-filtration apparatus. (The Versapore filter should be washed and dried by the same procedure as the sample (see below) prior to

taring). Wash the precipitate with three 10- to 30-ml portions of boiling water, two or three 10-ml portions of 95 percent ethanol, and with three 10-ml portions of diethyl ether to dry and distribute the precipitate over the filter pad.

6.16 Remove the dry filter and place in a heated (100°C) vacuum desiccator for 5–10 min (no longer). Remove, cool in a desiccator, and weigh. Mount in a ring-and-disk assembly, covering the precipitate with a thin plastic kitchen-type wrap.

6.17 Count the sample for three 50-min periods in a low-background beta counter.

7. Calculations

7.1 Ruthenium-106 efficiency factor (E): Counting efficiency for ruthenium-106 is determined by measurement of the count rate of standards prepared by direct precipitation of ruthenium metal from aliquots of the ruthenium-carrier solution spiked with known amounts of ruthenium-106. Ruthenium is reduced by metallic magnesium, filtered, dried, weighed, and counted as in the procedure above. Since recovery is usually in excess of 90 percent for the entire analytical procedure, the counting efficiency on the directly prepared standards is a reasonably accurate measurement of the counting efficiency of the samples. A typical value is 1.0 cpm/pCi.

7.2 Calculation of ruthenium-106 concentration: Use equation 1. The ruthenium recovery factor (f) is determined from the initial and final weights of ruthenium carrier.

pCi/l of ruthenium as ruthenium-106

$$= \frac{1000c}{KVEf(e^{-\lambda t})}. \qquad (1)$$

8. Report

Report ruthenium-106 values of less than 10 pCi/l to one significant figure. Values greater than 10 pCi/l are reported to two significant figures.

9. Precision

Typical ruthenium-106 values for the precision of this method are ±4 pCi/l or ±20 percent, whichever is larger, at the 95-percent confidence level.

References

Glendenin, L. E., 1951, Improved determination of ruthenium activity in fission, *in* Coryell, C. D., and Sugarman, N., Radiochemical studies: The fission products (Book 3): New York, McGraw-Hill Book Co., Paper no. 260, p. 1549.

Wyatt, E. I., and Richard, R. R., 1961, The radiochemistry of ruthenium: Natl. Acad. Sci., Natl. Research Council Nuclear Sci. Ser. NAS–NS 3029, 78 p.

Strontium-90, dissolved
Chemical separation and precipitation method (R-1160-76)

Parameter and code: Strontium-90, dissolved (pCi/l): 13503

1. Application

The method is applicable to all natural freshwaters and saltwaters. It is applicable to reactor wastes and may be applicable to industrial wastes, provided that recovery tests are made to assure that organic matter does not hold back strontium.

2. Summary of method

This method is based on the work of Hahn and Straub (1955) and of Johnson and Edwards (1967). Dissolved radiostrontium is determined by beta counting after a lengthy separation procedure that removes other fission products. Stable strontium carrier is added to the sample, and a carbonate precipitation is made to collect strontium-90 accompanied by some fission products. The carbonate precipitate is dissolved, and strontium nitrate mixed with calcium nitrate is precipitated with fuming nitric acid. Calcium is removed by washing with acetone, and strontium nitrate is further purified by solution and reprecipitation.

The precipitate may still contain traces of fission products such as transition metals, rare earths, niobium, zirconium, yttrium, and barium. Radium may be present. These are all removed by the addition of iron and barium carriers which are precipitated as the hydroxide and chromate respectively.

Final purification is effected by precipitating strontium as the oxalate. Yttrium-90, the radioactive daughter of strontium-90, has been completely removed at this point, and a new equilibrium begins. The yttrium isotope is also a beta emitter, and the sensitivity of the analysis is improved by counting after 21 d to allow in-growth of yttrium-90.

If strontium-89 is present, it is counted as strontium-90. Approximately 45 percent of the original strontium-89 activity is retained 21 d after the initial precipitation. Strontium-90 may be determined independently by chemically separating the yttrium-90 daughter, and relating its activity back to strontium-90. The composition of a mixture of the three isotopes, strontium-90, strontium-89, and yttrium-90, may be determined approximately by plotting the growth of radioactivity with time as shown in Johnson and Edwards (1967).

3. Interferences

Interferences from both fission products and natural radioactivity are negligible (Glendenin, 1951). As indicated above, strontium-89 is counted as strontium-90.

4. Apparatus

4.1 *Filter disks*, 25-mm Whatman No. 42, or equivalent.

4.2 *Filtration apparatus* for 25-mm membrane filters.

4.3 *Hotplate.*

4.4 *Low-background counter*, an anticoincidence-type counter with 2-in. thin window flowing gas proportional detector preferably capable of measuring both alpha and beta activity simultaneously.

4.5 *Ring-and-disk mounting assemblies for filters*, including 21-mm diameter rigid copper backing disks.

5. Reagents

5.1 *Acetic acid*, 6 *M*.

5.2 *Acetone*, anhydrous.

5.3 *Aluminum foil*, 3.5 mg/cm² or less.

5.4 *Ammonium acetate*, 6 *M* solution.

5.5 *Ammonium hydroxide*, concentrated and 6 *M*.

5.6 *Ammonium oxalate*, saturated solution.

5.7 *Barium carrier solution*, 1 ml=3.00 mg Ba^{+2}: Dissolve 1.33 g of $BaCl_2 \cdot 2H_2O$ in distilled water. Add a few drops of concentrated nitric acid and dilute to 250 ml.

5.8 *Diethyl ether*.

5.9 *Ethanol*, 95 percent.

5.10 *Iron carrier solution*, 1 ml=5 mg Fe^{+3}: Dissolve 500 mg of pure iron wire in a slight excess of nitric acid, and dilute to 100 ml.

5.11 *Nitric acid*, fuming, concentrated, 6 *M* and 1 *M*.

5.12 *Phenolphthalein indicator solution*.

5.13 *Sodium carbonate solution*, 1 *M* and 0.1 *M*.

5.14 *Sodium chromate solution*, 1.5 *M*.

5.15 *Strontium carrier solution*, 1 ml=4.00 mg Sr^{+2}: Dry "anhydrous" strontium nitrate overnight at 105°C, and cool in a desiccator. Weigh out 9.66 g of the dried salt, and dissolve in distilled water. Add 2 ml of concentrated nitric acid, and dilute to 1 liter. A more exacting procedure is described by Glendenin (1951, p. 1461), but the added work is not warranted unless the strontium nitrate contains radioactive impurities which contribute significantly to the reagent blank.

5.16 *Strontium-90 standard solution:* Strontium-90 standard solutions calibrated to ±1.5 percent are commercially available. In purchasing standards it is essential that the concentration of the stable isotopic carrier be known. Dilute the standard to approximately 5 pCi/ml as described by Barker and Robinson (1963, p. A28). It is generally necessary to add both acid and inactive strontium carrier at the time of dilution. The final solution should be approximately 0.1 *N* in hydrogen ion (HCl or HNO_3) and should have a chemical strontium carrier concentration of 0.1 to 10 mg/1. Strontium-90 standard activity (A), after a decay time (t_n), for an initial activity (A_o), can be calculated by use of the following equation:

$$A = A_o e^{-\lambda_n t_n},$$

where

λ_n = decay constant of strontium-90 (1.999×10^{-3} months^{-1}), and

t_n = elapsed time (in months) between certification of standard and time of count.

5.17 *Thymolphthalein indicator solution*.

6. Procedure

A reagent blank should be run with each set of samples to check for contamination of reagents, and to permit an accurate blank correction to be made. Occasional spiked samples (samples containing a known amount of added standard) should also be run through the entire procedure as checks.

6.1 To a 1,000-ml or other suitable aliquot of filtered water sample in a 1,500-ml beaker add 20 mg of strontium carrier (5 ml of 4-mg Sr^{+2}/ml). Heat to boiling on a hotplate. Make the solution basic to thymolphthalein indicator (blue color) by dropwise additions of concentrated ammonium hydroxide, and add an additional 6 ml.

6.2 Add 15 ml of 1.0 *M* sodium carbonate. Stir thoroughly, cover the beaker with a watch glass, and digest on a steam bath for 1 hr. Add more ammonium hydroxide, if required, to maintain the blue color of thymolphthalein. (Add more indicator if the color fades.)

6.3 Remove the beaker from the steam bath, and allow the precipitate to settle while the solution cools to room temperature.

6.4 Carefully decant or draw off as much as possible of the supernatant solution without disturbing the precipitate. Transfer the insoluble material to a 50-ml Pyrex centrifuge tube, and police the beaker with 0.1 *M* sodium carbonate. Add washings to the centrifuge tube. Centrifuge and discard the supernatant liquid.

6.5 Cautiously add 1 *N* nitric acid dropwise until the carbonate precipitate is com-

pletely dissolved. Dilute to 5 ml with distilled water. (Note: There may be a small residue of silica or insoluble metal oxide remaining.) Very cautiously add 25 ml of fuming nitric acid (work in the hood, use plastic gloves, safety goggles or face shield, and avoid inhaling the vapors!). Cool, stir, and centrifuge.

6.6 Using the above safety precautions, pour off the nitric acid as completely as possible, cool the tube below room temperature using cold water or ice bath, and cautiously add 25 ml of anhydrous acetone to the residue. Stir thoroughly and centrifuge, again discarding the supernate.

6.7 Repeat step 6.6.

6.8 Dissolve the nitrates in 5 ml of distilled water, and place the tube in a boiling-water bath until the odor of acetone is gone. (Caution: be sure acetone is completely removed.)

6.9 Cool below room temperature, and again precipitate strontium nitrate by adding 25 ml of fuming nitric acid. Swirl, cool, and centrifuge. Discard the supernate.

6.10 Dissolve the precipitate in 10 ml of distilled water and add 5 mg of ferric carrier (1 ml of 5-mg Fe^{+3} per ml) and 15 mg of barium carrier (5 ml of 3-mg Ba^{+2} per ml). Add concentrated ammonium hydroxide with constant stirring until ferric hydroxide begins to precipitate. Then add several drops excess. Centrifuge, and decant the supernate into a clean centrifuge tube. This operation removes the yttrium daughter of strontium-90. Record the time and date.

6.11 Add phenolphthalein indicator, and add 6 *N* nitric acid dropwise until the pink color disappears. Add 1 ml of 6 *N* acetate acid and 2 ml of 6 *M* ammonium acetate. Place the samples in a boiling-water bath and add 1 ml of 1.5 *M* sodium chromate while agitating. Leave in the water bath for 5–10 minutes.

6.12 Cool to room temperature, centrifuge, and decant the supernate into a 100-ml beaker. Discard the precipitate.

6.13 Add 2 ml of concentrated ammonium hydroxide, and heat to boiling. Add 5 ml of saturated ammonium oxalate solution and stir. Allow the precipitate to settle and the solution to cool to room temperature.

6.14 Filter through a tared 25-mm filter paper (Whatman, No. 42) supported on a sintered glass disk of a microanalytical filtration assembly. Wash the precipitate with three 5-ml portions of distilled water and then successively with small volumes of 95 percent ethanol and diethyl ether. Dry in a desiccator. Weigh as strontium oxalate monohydrate, and determine the gravimetric yield.

6.15 Mount the filter on a copper disk, 21-mm diameter. Cover with aluminum foil (3.5 mg/cm² or less). Store the sample for 21 d to permit in-growth of yttrium-90 to 99.5 percent of equilibrium activity. If it is desired to break down the activity into the three radioactive isotopes, it is necessary to start the counting within a few days of step 6.15 so that the decay of strontium-89 and in-growth of yttrium-90 may be observed.

6.16 Count the sample for 100 min on a low-background, anticoincidence shielded beta counter.

7. Calculations

7.1 Strontium-90 efficiency factor (E) and fractional chemical recovery (f_n): Use equation 2. Determine f_n from the weight of strontium oxalate.

$$E = \frac{\bar{c}_n}{d_n f_n \, (e^{-\lambda t_n})}, \qquad (2)$$

where

λ = decay constant of strontium-90 (1.999×10^{-3} month^{-1}).

7.2 Calculation of strontium-90 concentration: Use equation 1, making the decay correction if necessary. Determine f from the weight of strontium oxalate precipitate.

$$\text{pCi/l of strontium-90} = \frac{1{,}000\,\bar{c}}{KVEf \, (e^{-\lambda t})}. \qquad (1)$$

According to Hahn and Straub (1955), the chemical recoveries range from approximately 72 to 80 percent. Accurate determination of chemical recovery requires knowledge of the natural strontium content of the

sample. Normally this is less than 1 mg/l and may be neglected. In a few cases, particularly with waters from an area extending through parts of Wisconsin and Illinois, the strontium content may equal or exceed the strontium carrier added, and natural strontium must be determined for the calculation of chemical recovery.

7.3 Calculation of strontium-90, yttrium-90 and strontium-89. The count rate is determined at intervals over a timespan of approximately 30 d starting as close to zero time as possible. A typical counting schedule thereafter would be at 24 hr, 48 hr, 100 hr, 200 hr, and 400 hr. The count rates are plotted against time, and the curve thus obtained is compared against type curves for different isotopic ratios of strontium-90 to strontium-89 (Johnson and Edwards, 1967) to obtain the ratio for the sample.

8. Report

Report strontium-90 equivalent activities to ±0.5 pCi/l or to ±10 percent, whichever is greater.

9. Precision

Minimum detection level is 0.5 pCi/l and this is also the precision at activities below 5 pCi/l. At higher strontium-90 activities the precision is ±10 percent.

References

Barker, F. B., and Robinson, B. P., 1963, Determination of beta activity in water, U.S. Geol. Survey Water-Supply Paper 1696–A.

Glendenin, L. E., 1951, Determination of strontium and barium activities in fission, *in* Coryell, C. D., and Sugarman, N., eds., Radiochemical studies: The fission products, National Nuclear Energy Series IV, 9, Paper no. 236: New York, McGraw-Hill, p. 1460–69.

Hahn, R. Z., and Straub, C. P., 1955, Determination of radioactive strontium and barium in water: Am. Water Works Assoc. Jour., v. 47, p. 335–340.

Johnson, J. O., and Edwards, K. W., 1967, Determination of strontium-90 in water: U.S. Geol. Survey Water-Supply Paper 1696–E, 10 p.

Tritium
Liquid scintillation method, Denver lab (R-1171-76)

Parameters and codes: Tritium dissolved (pCi/l): 07005
Tritium, in water molecules (Tu): 07012

1. Application

The technique is generally applicable to the determination of tritium artificially introduced into water by such activities as tracer experiments, nuclear power, waste disposal, and thermonuclear weapons testing. The technique is not sufficiently sensitive to be applicable to the determination of very low natural tritium levels.

2. Summary of method

Liquid scintillation counting is based on the conversion of the energy of a particle emitted by a radioactive nucleus to light energy by means of a scintillating chemical. The scintillations are detected by a photomultiplier (PM) tube. The electrical signals from the PM tube are amplified and sent through a simple multichannel analyzer (three or four channels at most) where sorting into energy takes place. The counts in each channel are displayed on a scaler and may be read out on paper tape, punched tape, or magnetic tape.

Liquid scintillation counting is primarily used for the counting of beta emitters although it can also be used for alpha-emitting isotopes.

When liquid scintillation counting is used to determine a radionuclide in aqueous solution, the water sample is dissolved or dispersed in a large volume of organic solvent containing the scintillating chemical. A widely used mixture for aqueous solutions was dioxane-naphthalene containing the scintillator 2,5-diphenyloxazole (PPO) and a secondary scintillator used to shift the wavelength of the scintillations to the most sensitive spectral region of the PM tube. Much of the tritium data reported in the literature was determined by use of the above scintillation mixture. The dioxane-PPO combination has been superseded by proprietory scintillators that produce gels when mixed with water in proper ratios. The newer scintillators have approximately doubled the sensitivity of liquid scintillation counting for tritium. Since the composition of the proprietory mixtures is not available, these are listed by trade name in the "Reagent" section.

While the mechanism of liquid scintillation counting is not completely understood, it seems clear that the energy transfer is a two-stage process, with initial energy transfer to the solvent followed by transfer from the solvent to the scintillator. Many substances, including water, interfere in the energy transfer process to quench the scintillations and reduce the count rate. Excessive salt content, certain metals, and organic compounds quench in varying degree. Colored substances may quench by light absorption in addition to interfering with energy transfer. Quenching substances are generally removed by vacuum distillation.

The quenching effect of water is compensated by using a constant volume of water and constant ratio of water sample to scintillator mixture in both samples and standards. The count rate of a particular sample depends on both the volume of sample and the ratio of liquid scintillator mixture to

water sample. As the fraction of water sample in the water scintillator mixture increases, count rates increase until a point is reached where the quenching effect of the additional tritiated water exceeds the effect of the increased radioactivity. It is found that a practical compromise between maximum sample volume and scintillator volume provides optimum sensitivity. The maximum on the curve of activity versus volume of tritiated water (in a constant overall volume) is a rounded plateau. Therefore, the proportion of water sample to scintillating liquid mixture is not critical and is easily reproducible in routine work.

The permissible ratio of water sample to liquid scintillator mix is also controlled by physical stability of the gel formed.

A detailed description of the method is given by Schroder (1971).

3. Interferences

Distillation is used to remove both quenching substances and radionuclides that could contribute to excess count. Distillation is fully effective in removing inorganic salts and high-boiling organic compounds. Organic materials that vaporize at a lower temperature than water and are condensable under the same conditions as water vapor may be carried over in the vacuum distillation. If these materials contribute either quenching or beta radioactivity the possibility of interference exists, although it would appear remote.

Further protection against interferences is provided by the energy discrimination in the liquid scintillator analyzer and the external standard-ratio test.

4. Apparatus

4.1 *Autopipet*, 25-ml maximum capacity.

4.2 *Counting equipment.* Liquid scintillation spectrometer; counting systems capable of meeting the following specifications:

Counting efficiency—not less than 24 percent with optimum sample-scintillator mixture and polyethylene vials.
Background—not to exceed 5 cpm at sea level in tritium channel.
Sample capacity—at least 100 samples.
Operation—programmable and automatic.
Internal check—an external standard and ratio computation capability required.
Readout—automatic printout.

4.3 *Pipets*, 8 ml.

4.4 *Vacuum-distillation apparatus.* Consists of a 50-ml round-bottom flask as the distillation flask and a 125-ml round-bottom flask as the condenser flask. The distillation flask is heated with a rheostat-controlled mantle, and the condenser flask dips into a Dewar containing isopropanol-dry ice. The two flasks are connected by a 20-mm diameter U-tube, 10-cm long with ground-glass connectors and stopcock for application of vacuum. Heating tape is coiled around the U-tube connecting the two flasks.

5. Reagents

5.1 *Scintillator*, Instagel (Packard Instrument Co.) for low-temperature counting (1°–4°C). A preblended gel-forming scintillator designated 3A70* (Research Products International) for room-temperature counting.

5.2 *Tritium standard solution:* Appropriate standards are prepared by the dilution of NBS standard tritiated water with "dead" water, that is, water containing less than 1 Tu.

5.3 *Water, "dead."* The tritium blank introduced by reagents must be tested at intervals by analyzing "dead" water (water with no measurable tritium content) in exactly the same procedure as for a normal water sample. It is very difficult to confirm that a water is truly "dead," and it is usually necessary to make the assumption that water from a deep well in a confined aquifer a hundred kilometers or more from the recharge area is "dead." This assumption can be correct only if the well is pumped sufficiently to expel all meteoric water that may have entered the well and surrounding aquifer by leakage.

6. Procedure

6.1 Counting.

6.1.1 Distill 25 ml of water sample for direct counting, or approximately 10 ml of

electrolyzed water sample, using the vacuum distillation apparatus. The U-tube is preheated to assure dryness.

6.1.2 Pipet 8.00 ml of the distillate from the preceding step into a 25-ml polyethylene vial, and add 14 ml of scintillator mix. The choice of scintillator depends on the type of liquid scintillation spectrometer to be used for counting. Instagel is used with the instruments that operate at cold temperature (3°C), and 3A70* is used with the instruments that operate at room temperature. Cap the vial and mix. Heat the Instagel-sample mixture on a hotplate at approximately 100°C for 2 or 3 min. This clarifies the mixture. The 3A70*-sample mixture does not require heating. The above operation is carried out under subdued red light to filter out the blue region of the spectrum. This minimizes excitation of fluorescence background in the sample.

6.1.3 Prepare three blanks and two standards in the same manner as the samples. Place one standard in the 2d counting position in the spectrometer and one in the 10th position. Place blanks at intervals throughout the run of 10–14 samples.

6.1.4 Place three sealed standards (triated toluene in glass-sealed scintillator solution) in the group. One standard goes in the first counting position to permit monitoring the instrument before counting the samples. The remaining sealed standards are placed near the blanks.

6.1.5 Allow prepared samples to remain in the dark in the liquid scintillation spectrometer for several hours before counting begins. This allows decay of fluorescence and chemiluminescence. A minimum of 8 hr standing is required with Instagel and 12 hr with 3A70*.

6.1.6 Count each vial five times for 100 min. Total counting time for one sample is 500 min. Counting time is reduced for very active samples. One million counts is cutoff setting.

6.1.7 Program the instrument to perform the external-standard ratio analysis on samples, standards, and blanks at the end of the counting run (see instrument instruction manual). This procedure is a check for quenching. The ratio of low-energy counts in channel A of the spectrometer is established for both tritium and an external standard placed near the sample vial. The value of R in the following equation should be constant to within ± 0.2.

$$R = \left[\frac{\text{Counts in A}}{\text{Counts in B}}\ \text{tritium}\right] \left[\frac{\text{Counts in B}}{\text{Counts in A}}\ \text{standard.}\right].$$

Individual samples that fall outside this range must be reanalyzed. If all values of R fall outside this range, the scintillator has deteriorated and must be replaced.

7. Calculations

Several statistical schemes have been presented for the calculation and verification of tritium data, each intended to optimize a particular analytical situation. In the present analytical procedure the repeated counting of individual samples has the effect of averaging out short-term fluctuations. Statistical checks have shown that highest precision, in this analytical situation, is attained by the use of longer term average values for the samples and standards.

Counting efficiency and background values are determined with tritium standards whenever a new lot of scintillator is used. Counting-efficiency data and background data from standards and blanks run with each set are also determined. The new data from each set are averaged into the data from the preceding sets, thus creating a moving average value for counting efficiency and background. As new efficiency and background data appear they displace older data entered into the moving average. Data from four or five valid runs (no quenching or other aberration) enter into the moving average used at any given time.

7.1 Tritium efficiency factor (E). Use equation 2:

$$E = \frac{\bar{c}_n}{d_n(e^{-\lambda t_n})}, \qquad (2)$$

where

$\overline{c}_s$ = average count rate of standard (cpm) corrected for background and blank,

d_s = disintegration rate of standard (dpm), corrected for blank ($\overline{S} - \overline{B}$),

λ = decay constant of tritium (4.685×10^{-3} month^{-1}),

t_s = elapsed time between certification of the standard and time of count in same units as λ,

where

$\overline{S}$ = moving average count rate (cpm) of the standards, and

$\overline{B}$ = moving average count rate (cpm) of the blanks.

7.2 Calculation of tritium concentration: Use equation 1. The chemical recovery factor (f) is an enrichment factor when electrolytic enrichment is applied to the sample. Since electrolysis is not used the value of f is unity.

$$\text{pCi tritium/l} = \frac{1{,}000}{KVEf(e^{-\lambda t})}, \quad (1)$$

where f is electrolytic enrichment factor determined by standard included in the run,

$$f = \frac{\text{cpm/ml after electrolysis}}{\text{cpm/ml before electrolysis}}.$$

7.3 Conversion of tritium concentration in pCi/l to tritium units. Tritium concentration in Tu $= \frac{\text{pCi tritium/l}}{3.22}$.

8. Report

Concentrations in both tritium units and picocuries per liter are reported to two significant figures down to the minimum detection level (MDL). The latter can only be estimated because of the very pronounced effect of altitude on the background count. At sea level the MDL is estimated at 60 Tu, and at 5,000 ft (1,500 m) it is estimated at 150 Tu for the direct count method.

9. Precision

Precision is dependent on altitude in the same way as MDL. At 500 Tu reproducibility is approximately ±20 percent. Precision improves with increasing concentration.

Reference

Schroder, L. J., 1971, Determination of tritium in water by the U.S. Geological Survey, Denver, Colo.: U.S. Geol. Survey Rept. USGS–474–134, 22 p.; Avail. *only* from U.S. Dept. Commerce, Natl. Tech. Inf. Service, Springfield, VA 22151.

Tritium
Liquid scintillation method, Reston lab (R-1173-76)

Parameters and codes: Tritium, dissolved (pCi/1): 07005
Tritium, in water molecules (Tu): 07012

1. Application

The technique can be used directly to analyze waters containing more than 60 Tu (190 pCi/l). Many natural-water samples contain less than 60 Tu so the tritium in such samples is normally enriched by electrolysis (method R-1174-76) before they are analyzed by this technique.

The direct liquid scintillation counting method, while useful for analysis of the tritium introduced into water by rainout in some samples, is primarily used for measuring tritium introduced in tracer tests and locally by nuclear power and waste disposal facilities.

2. Summary of method

Liquid scintillation counting is based on the conversion of the energy of a particle emitted by a radioactive nucleus to light energy by means of a scintillating chemical. The scintillations are detected by a photomultiplier (PM) tube. The electrical signals from the PM tube are amplified and sent through a two or three channel analyzer where sorting by energy ranges takes place. The counts in each channel are displayed on a scaler and are printed and(or) read out on punched tape or magnetic tape. In order to minimize spurious counts, from cosmic radiation or electrical noise inherent in the PM tubes themselves, for example, two PM tubes are used to detect the scintillations. The two tubes are operated in concidence, so that only if a scintillation event is detected by both tubes simultaneously is a signal sent on to the energy analyzer and scalar circuitry.

When liquid scintillation counting is used to determine a radionuclide in aqueous solution, the water sample is dissolved or dispersed in a larger volume of organic solvent containing the scintillating chemical. A widely used mixture for aqueous solutions was dioxane-naphthalene containing the scintillator 2,5-diphenyloxazole (PPO) and a secondary scintillator used to shift the wavelength of the scintillations to the most sensitive spectral region of the PM tube. Much early tritium data was determined by use of the above scintillation mixture. The dioxane-PPO combination has been superseded by proprietory scintillators that produce gels when mixed with water in proper ratios. The newer scintillators have approximately doubled the sensitivity of liquid scintillation counting for tritium. These solutions generally include an organic solvent (toluene or xylene, for example) in which the scintillator is dissolved, plus a strong liquid detergent to promote emulsification between the sample water and the scintillator-containing organic solvent.

Since the exact composition of the proprietory mixtures is not available, these are listed by trade name in the reagent section.

While the mechanism of liquid scintillation counting is not completely understood, it seems clear that the energy transfer is a two-stage process, with initial energy transfer to the solvent followed by transfer from the solvent to the scintillator. Many

substances, including water, interfere in the energy transfer process to quench the scintillations and reduce the count rate. Excessive salt content, certain metals, and organic compounds quench in varying degree. Colored substances may quench by light absorption in addition to interfering with energy transfer. Quenching substances are generally removed by vacuum distillation.

The quenching effect of water is compensated by using a constant volume of water and constant ratio of water sample to scintillator mixture in both samples and standards. The count rate of a particular sample depends on both the volume of sample and the ratio of liquid scintillator mixture to water sample. As the fraction of water sample in the water scintillator mixture increases, count rates increase until a point is reached where the quenching effect of the additional tritiated water exceeds the effect of the increased radioactivity. It is found that a practical compromise between maximum sample volume and scintillator volume provides optimum sensitivity. The ratio of sample to scintillator solution (in a constant total volume) can vary slightly without affecting the counting characteristics of the mix. Thus optimally sensitive mixes can be produced in routine work.

The permissible ratio of water sample to liquid scintillator mix is also controlled by physical stability of the gel formed. A detailed description of the method is given by Schroder (1971), and the counting characteristics and thermal stability of various water-scintillator solution mixtures are given in the manufacturers' literature.

3. Interferences

Potential interferences come from other radionuclides or quenching substances present in the sample. Both types are removed by vacuum distillation of the sample before preparation of the counting mixture.

A rare ground-water sample may contain radon-222 in an amount large enough to persist in the sample even after distillation. Some radon decay is counted in the tritium energy channel and leads to spuriously high results. Radon has a short half-life (3.8 d) and its presence is obvious from a decline in count rate while a sample is counted over a period of several days or a week.

A radon-containing sample can be purified by distilling it to remove any parent radium-226, allowing the sample to stand for 3–4 weeks for the radon to decay, and redistilling before counting to remove the radon daughter lead-210.

The analysis of tritium in highly radioactive samples, such as those from nuclear facilities, may be confused by the presence of other radioactive noble gases, particularly krypton-85 and argon-41. Rhinehammer and Lamberger (1973) discuss techniques for tritium analysis in the presence of concentration of other radioisotopes much higher than found in natural samples.

Samples prepared for counting by electrolytic enrichment are normally free of radioactive or quenching interfering substances.

4. Apparatus

4.1 *Counting equipment,* liquid scintillation spectrometer, with two PM tubes, operating in coincidence minimum of two channels for pulse-energy analysis; automatic sample changer, minimum 100 samples; constant temperature chamber for PM tubes and shield and sample changer, adjustable to as low as 0°C; readout device(s) to paper for visual inspection of results and to punched tape or other automatic data processing (ADP) compatable form for data transfer to computer for final calculations. Optional: automatic external standardization by channels-ratio method for quench determination. Properly prepared samples do not differ in quenching, and this determination is unnecessary. The presence of the external standard source near the counting chamber may add additional background.

Counters as received from the manufacturer will not normally be adjusted for optimum counting of water mixtures, and before routine tritium measurements are be must be carefully adjusted in the laboratory

gun. Adjustments are possible to: PM-tube high voltage; amplifier gain; energy analyzing channel limits; and (by a manufacturer's representative) the time interval in which a pulse in one PM tube is taken as simultaneous with a pulse in the other and sent on to the analyzer circuitry.

The type of scintillator solution and optimum water to solution ratio of the counted mixture must also be chosen, and the counting-chamber temperature set as low as possible to minimize PM-tube noise without causing the counted mixture to separate or freeze.

The utility of a liquid scintillation spectrometer for low-level counting is determined by its background count rate and its tritium-counting efficiency. A frequently used counting mixture consists of 12 ml H_2O sample plus 13 ml Insta-Gel (Packard Instrument Co.), in a polyethylene vial. Presently available (1976) commercial counters are capable of counting this mixture, with efficiences of 20 percent or greater, and backgrounds of 3.6 cpm or less. Older instruments, with efficiences as low as 12 percent and backgrounds as high as 3.8 cpm, may also be satisfactory, but will require longer counting times.

4.2 *Counting vials,* commercial, screw-cap polyethlyene liquid scintillation counting vials, with caps with reflective liners.

4.3 *Vacuum-distillation apparatus.*

4.4 *Miscellaneous glassware,* pipets for preparing counting mixtures, standard solutions, and so forth.

4.5 *Analytical balance.*

5. Reagents

5.1 *Scintillator,* commercial solutions for counting water mixtures, such as: Insta-Gel, Packard Instrument Co.; Ready-Soln, Beckman Instrument Co.; Scintillator 3A70*, Research Products International; Scinti Verse, Fisher Scientific Co.; Aquasol, Nuclear Associates; or ScintillAR, Malinkrodt Chemical Co.

5.2 *Tritium standard solution:* Appropriate standards for determining counter efficiency are prepared by the dilution of NBS standard tritiated water with "dead" water, that is, water containing less than 1 Tu. A standard containing 50 to 100 dpm/ml tritium (7 to 15×10^3 Tu) is adequate.

5.3 *Water, "dead".* Water with no measurable tritium ("dead" water) is required for determination of counter-background rate and for dilution of standard tritiated water. It is very difficult to confirm that a water is truly "dead," and it is usually necessary to make the assumption that water from a deep well in a confined aquifer a hundred kilometers or more from the recharge area is "dead." This assumption can be correct only if the well is pumped sufficiently to expel all meteoric water that may have entered the well and surrounding aquifer by leakage.

6. Procedure

6.1 Distillation. Samples enriched by electrolysis are distilled in the final step of that procedure and require no further treatment before preparing the counting mixture. All other samples must be vacuum distilled before preparing the counting mixture.

6.2 Counting. Samples are counted in sets, each requiring about 1 week of counting. A set typically includes 1 standard, 1 or 2 blanks (backgrounds), and from 7 to 15 samples. The number of samples per set depends on tritium content. Low-tritium samples require longer counting times, and so fewer can be counted per week.

Members of a count set are prepared together and in the same way. The proper volumes of sample, standard, or "dead" water is pipetted into a tared counting vial and its mass determined to ±0.01 g. The scintillation solution is then added by manual or autopipet. The water to scintillator solution ratio must be constant within a count set for the optimized counter settings. If sufficient sample volume is not available, following electrolysis, for example, the mass of sample in the counting vial is first measured, then "dead" water added to bring the total water volume to that required by the counter settings.

The vials are capped and the contents thoroughly mixed. Heating the mixture to

40°–60°C promotes emulsification, but is not necessary. The set is then placed in the counter sample changer for at least 24 hr before counting begins to reach thermal equilibrium and for chemiluminescence (if any) to decay.

Members of each set are counted sequentially for a preset time (40 to 100 min) or until a preset number of counts (5,000 to 10,000) have accumulated. The counter then records the sample number, count time, and counts accumulated, and moves the next sample into position. After the last sample, the sample changer returns to the first sample and the cycle repeats.

If the automatic external-standardization option on the counter is used, the standardization is done at the end of each count on each sample and the results recorded before changing to the next sample.

The total time required for counting a sample is determined by its tritium content (see sec. 7.3 below). If a set contains several high-tritium samples, these can be removed individually when they have counted long enough, and counting of the remainder of the set continued.

7. Calculations

7.1 Tritium counting efficiency (E). Use equation 2:

$$E=\frac{\overline{c}_s}{d_s(e^{-\lambda t_s})\times V_s}, \qquad (2)$$

where

$\overline{c}_s$ = average count rate of standard (cpm) above background ($\overline{S}-\overline{B}$),

d_s = disintegration rate of standard (dpm/g),

V_s = mass of standard counted (g),

λ = decay constant of tritium (1.534×10^{-4} d^{-1}),

t_s = elapsed time between certification of the standard and time of count in same units as λ,

where

$\overline{S}$ = average count rate (cpm) of the standard in the set, and

$\overline{B}$ = average count rate (cpm) of the blank(s), (backgrounds) in the set.

7.2 Calculation of tritium concentration. Use equation 1:

$$\mathrm{Tu}=\frac{\overline{C}}{KVEf\,(e^{-\lambda t})}, \qquad (1)$$

where

$\overline{C}$ = average sample count rate above background (cpm),

V = mass of sample water counted (g),

E = counting efficiency, from equation 2, $\left[\frac{\text{cpm}}{\text{dpm}}\right]$,

f = electrolysis enrichment factor. For samples counted directly, $f=1$ (for calculations of f for electrolyzed samples, see method R–1174–76),

λ = decay constant of tritium (1.534×10^{-4} d^{-1}),

t = time elapsed between sample collection date and date counted, in same units as λ, and

$K=7.13\times10^{-3}$ dpm/g Tu.

7.3 Calculation of tritium counting error. The error term which accompanies tritium results is calculated such that there is a 67 percent probability that the true tritium content of the sample is in the range of the reported value ± the error term.

Errors of tritium analyses are due primarily to the uncertainty inherent in any attempt to measure the rate of occurence (count rate) of a random process (radioactive decay). For a count rate, R, the standard deviation $\sigma=R/t$, where t is the total count time. Errors in counting both the sample and background are included in the net sample count rate $\overline{C}$, above. That is, if $\overline{C}=\overline{S}-\overline{B}$,

$$\sigma\overline{C}=\sqrt{\sigma\frac{2}{\overline{S}}+\sigma\frac{2}{\overline{B}}}\ . \qquad (3)$$

In sets counted as described above, the counting time for background and sample are the same, so equation 3 can be written:

$$\sigma\overline{C}=\sqrt{(\overline{C}+2\overline{B})/t}. \qquad (4)$$

The relative error, or precision of the count rate measurement is:

$$\sigma\overline{C}/\overline{C}.$$

Thus equation 4 shows that analytical precision increases ($\sigma\overline{C}/\overline{C}$ becomes smaller) with longer count time, or, for a fixed count time, increases with higher sample count rates (a higher tritium-counting efficiency or a higher sample tritium concentration) or with a lower background count rate.

In addition to the count-rate error, small errors are associated with each of the other terms in equation 1, and the reported σ_{Tu} is calculated with the expression

$$\sigma_{Tu} = Tu \times \sqrt{\left(\frac{\sigma\overline{C}}{\overline{C}}\right)^2 + \left(\frac{\sigma v}{v}\right)^2 + \left(\frac{\sigma E}{E}\right)^2 + \left(\frac{\sigma f}{f}\right)^2} \quad (5)$$

There are also errors associated with the K and $(e^{-\lambda t})$ terms in equation 1, primarily due to uncertainties in the knowledge of the tritium half-life, but they are negligible for most purposes.

Because Tu-error calculations are tedious and complicated, they are done by computer from the counting data punched or otherwise directly recorded by the counter.

8. Report

Tritium errors are reported to two significant figures or to the nearest 0.1 Tu, whichever is larger. The tritium result itself is reported to the same number of significant figures.

Tritium data are frequently required in pCi/l rather than in Tu. To convert, use the expression:

$$PCi\ tritium/l = 3.2\ Tu.$$

9. Precision

The precision of tritium analyses varies with sample tritium content and with laboratory configuration and location. The one standard deviation (1σ) error is reported with each result. The calculation of this error is described above (sec. 7.3).

References

Schroder, L. J., 1971, Determination of tritium in water by the U.S. Geological Survey, Denver, Colo.: U.S. Geol. Survey Rept. USGS–474–134, 22 p.; Avail. *only* from U.S. Dept. Commerce, Natl. Tech. Inf. Service, Springfield, VA. 22151.

Rhinehammer, T. B., and Lamberger, P. H., 1973, tritium content technology, U.S.A.E.C. report WASH–1269, 292 pp. (Avail. from NTIS).

Tritium
Electrolytic enrichment—liquid scintillation method, Denver lab (R-1172-76)

Parameters and codes: Tritium, dissolved, (pCi/l): 07005
Tritium, in water molecules (Tu): 07012

1. Application

Gas counting preceded by electrolytic enrichment is the most sensitive analytical method for tritium and is applicable down to concentrations in the range of 1 Tu. With very careful control of ambient laboratory tritium levels, and a valid blank based on "dead" water, it is possible to apply the method to waters as low as 0.2 Tu. Where gas-counting equipment is not available or where a lower detection limit of 25 Tu is satisfactory, electrolytic enrichment followed by liquid scintillation counting permits the analysis at lower concentrations than by liquid scintillation alone (method R-1171-76). The technique also may be applied to samples having high concentrations of nonvolatile radioactivity contamination such as strontium-90, because the sample preparation steps eliminate solid materials.

The technique is generally applicable to determine tritium introduced into water by rainout and to measure natural levels of tritium in surface waters. The technique is not sufficiently sensitive for the determination of very low natural tritium levels.

2. Summary of method

When it is necesary to determine tritium at a lower concentration, with improved accuracy, than is available in the liquid scintillation method (R-1171-76), an electrolytic enrichment step is introduced ahead of the liquid scintillation counting. The electrolysis techniques were introduced by Kaufmann and Libby (1954).

Electrolytic enrichment is carried out by adding sodium peroxide (forms sodium hydroxide), followed by carefully controlled electrolysis in specially designed cells. The cells of Östlund and Werner (1961) are used. The isotopic fractionation factors are improved by operation at low temperature. Hence, the electrolysis is carried out while the cells are partially immersed in a cold bath maintained at a temperature just above freezing.

The percentage of recovery of tritium in the electrolysis is a complex function of temperature, current density, and electrode surface reactions which are not fully understood. Practical systems have been developed which achieve 70–80 percent recovery of tritium in electrolysis from approximately 500 to 10 ml. More extensive electrolysis provides greater enrichment but lower percentage of recovery. The reproducibility of recovery between electrolyses is approximately 3–4 percent under normal conditions.

Liquid scintillation counting is based on the conversion of the energy of a particle emitted by a radioactive nucleus to light energy by means of a scintillating chemical. The scintillations are detected by a photomultiplier (PM) tube. The electrical signals from the PM tube are amplified and sent through a simple multichannel analyzer (three or four channels at most) where sorting into energy takes place. The counts in

each channel are displayed on a scaler and may be read out on paper tape, punched tape, or magnetic tape.

Liquid scintillation counting is used primarily for the counting of beta emitters although it can also be used for alpha-emitting isotopes.

When liquid scintillation counting is used to determine a radionuclide in aqueous solution, the water sample is dissolved or dispersed in a larger volume of organic solvent containing the scintillating chemical. A widely used mixture for aqueous solutions was dioxane-naphthalene containing the scintillator 2,5-diphenyloxazole (PPO) and a secondary scintillator used to shift the wavelength of the scintillations to the most sensitive spectral region of the PM tube. Much of the tritium data reported in the literature was determined by use of the above scintillation mixture. The dioxane-PPO combination has been superseded by proprietory scintillators that produce gels when mixed with water in proper ratios. The newer scintillators have approximately doubled the sensitivity of liquid scintillation counting for tritium. Since the composition of the proprietory mixtures is not available, these are listed by trade name in the "Reagent" section.

While the mechanism of liquid scintillation counting is not completely understood, it seems clear that the energy transfer is a two-stage process, with initial energy transfer to the solvent followed by transfer from the solvent to the scintillator. Many substances, including water, interfere in the energy-transfer process to quench the scintillations and reduce the count rate. Excessive salt content, certain metals, and organic compounds quench in varying degree. Colored substances may quench by light absorption in addition to interfering with energy transfer. Quenching substances are generally removed by vacuum distillation.

The quenching effect of water is compensated by using a constant volume of water and constant ratio of water sample to scintillator mixture in both samples and standards. The count rate of a particular sample depends on both the volume of sample and the ratio of liquid scintillator mixture to water sample. As the fraction of water sample in the water-scintillator mixture increases, count rates increase until a point is reached where the quenching effect of the additional tritiated water exceeds the effect of the increased radioactivity. It is found that a practical compromise between maximum sample volume and scintillator volume provides optimum sensitivity. The maximum on the curve of activity versus volume of tritiated water (in a constant overall volume) is a rounded plateau. Therefore, the proportion of water sample to scintillating liquid mixture is not critical and is easily reproducible in routine work.

The permissible ratio of water sample to liquid scintillator mix is also controlled by physical stability of the gel formed.

A detailed description of the method is given by Schroder (1971).

3. Interferences

There are no interferences in the analytical method when electrolysis is included. Distillation is used to remove both quenching substances and radionuclides that could contribute to excess counts. Distillation and electrolysis are fully effective in removing inorganic salts, high-boiling organic compounds, and gaseous radioisotopes. Krypton and all other gases are stripped out in the electrolysis owing to prolonged bubbling of oxygen and hydrogen through the sample.

Further protection against interferences is provided by the energy discrimination in the liquid-scintillator analyzer and the external standard-ratio test.

4. Apparatus

4.1 *Autopipet*, 25-ml maximum capacity.

4.2 *Counting equipment.* Liquid scintillation spectrometer; counting systems capable of meeting the following specifications:

Background—not to exceed 5 cpm at sea level in tritium channel.

Counting efficiency—not less than 24 percent with optimum sample-scintillator mixture and polyethylene vials.

Sample capacity—at least 100 samples.
Operation—programmable and automatic.
Internal check—an external standard and ratio computation capability required.
Readout—automatic printout.

4.3 *Electrolysis unit.* Contains the following components:

4.3.1 Electrolysis cells. See figure 8. The Östlund cell has a mild-steel cathode (where reduction of hydrogen isotopes occurs) and stainless-steel anode. The glass envelope is designed to attach directly to a vacuum-distillation apparatus.

4.3.2 Power supply, direct current, at least 6 amperes at 30 volts.

4.3.3 Freezer, floor-model, large enough to hold two rows of five electrolysis cells.

4.3.4 Exhaust lines, to vent the explosive mixture of oxygen and hydrogen generated in electrolysis.

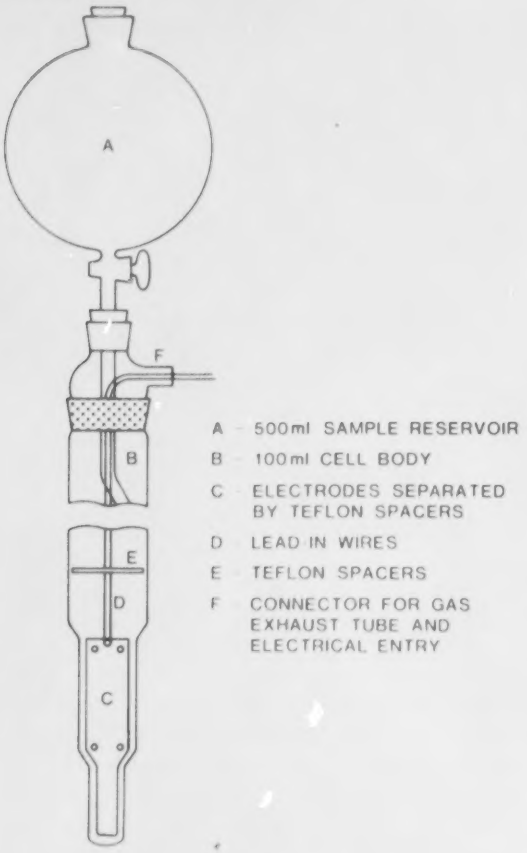


Figure 8.—Östlund electrolysis cell.

4.4 *Pipets,* 8-ml.

4.5 *Vacuum-distillation apparatus.* Consists of a 100-ml round-bottom flask as the distillation flask and a 125-ml round-bottom flask as the condenser flask. The distillation flask is heated with a rheostat-controlled mantle and the condenser flask dips into a Dewar containing isopropanol-dry ice. The two flasks are connected by a 20-mm diameter U-tube, 10-cm long with ground-glass connectors and stopcock for application of vacuum. Heating tape is coiled around the U-tube connecting the two flasks.

5. Reagents

5.1 *Scintillator,* Instagel (Packard Instrument Co.) for low-temperature counting (1°–4°C). A preblended gel-forming scintillator designated 3A70* (Research Products International) for room-temperature counting.

5.2 *Sodium peroxide,* reagent-grade.

5.3 *Tritium standard solution:* Appropriate standards are prepared by the dilution of NBS standard tritiated water with "dead" water, that is, water containing less than 1 Tu.

5.4 *Water, "dead":* The tritium blank introduced by reagents and leakage during electrolysis must be tested at intervals by analyzing "dead" water (water with no measurable tritium content), in exactly the same procedure as for a normal water sample. It is very difficult to confirm that a water is truly "dead," and it is usually necessary to make the assumption that water from a deep well in a confined aquifer a hundred kilometers or more from the recharge area is "dead." This assumption can be correct only if the well is pumped sufficiently to expel all meteoric water that may have entered the well and surrounding aquifer by leakage.

6. Procedure

6.1 Electrolysis. (In electrolysis and all other steps, heat-dried glassware is used.)

6.1.1 Distill 55-ml volume of water sample in the vacuum-distillation apparatus. The unit is evacuated before use, and the water

sample is protected from atmospheric moisture during distillation. Distill to dryness. Recovery is usually slightly less than the original volume because of water of hydration remaining in the salts residue and droplets on the walls of the apparatus. The tritium fractionation attributable to nondistilled water is insignificant.

6.1.2 Transfer the distillate to a clean and dry Östlund electrolysis cell (fig. 8), add 0.75 g of sodium peroxide, add 50 ml of the distilled-water sample, and stopper the cell. An argon atmosphere is maintained in the reservoir to eliminate contact with atmospheric moisture.

6.1.3 Prepare a blank sample ("dead" water) for electrolysis using the above procedure. Prepare a standard for electrolysis (200 Tu is a convenient concentration range) using the above procedure.

6.1.4 Set up one blank, one standard, and four samples in series in the electrolysis bath. A larger number of samples may be used if sufficient voltage is available from the electrolysis power supply. The tritium enrichment for one group of samples is determined by the enrichment of the standard in series with the group.

6.1.5 Proceed with the electrolysis after samples have been cooled in the cold chest. The temperature of the ethylene glycol-water coolant bath is maintained at 0°C throughout the process. Electrolysis from 50 ml to approximately 10 ml using 4-ampere current.

6.1.6 Neutralize the highly caustic solution in the cells to permit full recovery of tritium and to avoid mechanical and corrosion problems in subsequent steps. Disconnect a cell from the electrolysis line, and while protecting from the atmosphere insert a disposable pipet through the hole in the Teflon spacer. Bubble carbon dioxide through slowly. About 5 min and 1 liter of carbon dioxide are required to complete neutralization. A precipitate of sodium carbonate forms.

6.1.7 Distill the neutralized sample into a small tared Pyrex bulb using vacuum-distillation apparatus. The sample is cooled (but not frozen) in liquid nitrogen. Attach the still-liquid sample to the inlet of the distillation apparatus and apply vacuum. The sample first bubbles to release trapped gases and then freezes. Apply a heat lamp or heat gun to distill the sample into the liquid-nitrogen-cooled receiving bulb. Weigh the bulb after completion of distillation to determine the volume of the water sample collected.

6.2 Counting.

6.2.1 Pipet 8.00 ml of the distillate from the preceding step into a 25-ml polyethylene vial, and add 14 ml of scintillator mix. The choice of scintillator depends on the type of liquid scintillation spectrometer to be used for counting. Instagel is used with the instruments that operate at cold temperature (3°C) and 3A70* is used with the instruments that operate at room temperature. Cap the vial and mix. Heat the Instagel-sample mixture on a hotplate at approximately 100°C for 2 or 3 min. This clarifies the mixture. The 3A70*-sample mixture does not require heating. The above operation is carried out under subdued red light to filter out the blue region of the spectrum. This minimizes excitation of fluorescence background in the sample.

6.2.2 Prepare three blanks and two standards in the same manner as the samples. Place one standard in the 2d counting position in the spectrometer and one in the 10th position. Place blanks at intervals throughout the run of 10–14 samples.

6.2.3 Place three sealed standards (tritated toluene in glass-sealed scintillator solution) in the group. One standard goes in the first counting position to permit monitoring the instrument before counting the samples. The remaining sealed standards are placed near the blanks.

6.2.4 Allow prepared samples to remain in the dark in the liquid scintillation spectrometer for several hours before counting begins. This allows decay of fluorescence and chemiluminescence. A minimum of 8-hr standing is required with Instagel and 12 hours with 3A70*.

6.2.5 Count each vial five times for 100 min. Total counting time for one sample is 500 min.

6.2.7 Program the instrument to perform the external-standard ratio analysis on samples, standards, and blanks at the end of the counting run (see instrument instruction manual). This procedure is a check for quenching. The ratio of low-energy counts in channel A of the spectrometer is established for both tritium and an external standard placed near the sample vial. The value of R in the following equation should be constant to within ± 0.2.

$$R = \left[\frac{\text{Counts in A}}{\text{Counts in B}}\ \text{tritium}\right] \left[\frac{\text{Counts in B}}{\text{Counts in A}}\ \text{standard}\right].$$

Individual samples that fall outside this range must be reanalyzed. If all values of R fall outside this range, the scintillator has deteriorated and must be replaced.

7. Calculations

Several statistical schemes have been presented for the calculation and verification of tritium data, each intended to optimize a particular analytical situation. In the present analytical procedure the repeated counting of individual samples has the effect of averaging out short-term fluctuations. Statistical checks have shown that highest precision, in this analytical situation, is attained by the use of longer term average values for the samples and standards.

Counting efficiency and background values are determined with tritium standards whenever a new lot of scintillator is used. Counting-efficiency data and background data from standards and blanks run with each set are also determined. The new data from each set are averaged into the data from the preceding sets, thus creating a moving average value for counting efficiency and background. As new efficiency and background data appear they displace older data entered into the moving average. Data from four or five valid runs (no quenching or other aberration) enter into the moving average used at any given time.

7.1 Tritium efficiency factor (E). Use equation 2:

$$E = \frac{\bar{c}_n}{d_n(e^{-\lambda t_n})}, \qquad (2)$$

where

$\bar{c}_n$ = average count rate of standard (cpm) corrected for background and blank,

d_n = disintegration rate of standard (dpm), corrected for blank ($\bar{S} - \bar{B}$),

λ = decay constant of tritium (4.685×10^{-3} month^{-1}),

t_n = elapsed time between certification of the standard and time of count in same units as λ,

where

$\bar{S}$ = moving average count rate (cpm) of the standards, and

$\bar{B}$ = moving average count rate (cpm) of the blanks.

7.2 Calculation of tritium concentration: Use equation 1. The chemical recovery factor (f) is an enrichment factor when electrolytic enrichment is applied to the sample.

$$\text{pCi tritium/l} = \frac{1{,}000\bar{c}}{KVEf(e^{-\lambda t})}, \qquad (1)$$

where f is electrolytic enrichment factor determined by standard included in the run,

$$f = \frac{\text{cpm/ml after electrolysis}}{\text{cpm/ml before electrolysis}}.$$

7.3 Conversion of tritium concentration in pCi/l to tritium units.

$$\text{Tritium concentration in Tu} = \frac{\text{pCi tritium/l}}{3.22}.$$

8. Report

Concentrations in both tritium units and picocuries per liter are reported to two significant figures down to the minimum detection level (MDL). The latter can only be estimated because of the very pronounced effect of altitude on the background count. At 5,000 ft (1,500 m) it is estimated at 25 Tu for the liquid scintillation counting of an electrolytically enriched sample.

9. Precision

Precision is dependent on altitude in the same way as MDL. At 500 Tu reproducibility

is approximately ±20 percent. Precision improves with increasing concentration and is improved by electrolytic concentration of samples with lower tritium concentration.

Reproducibility for samples enriched by electrolysis is limited by the reproducibility of electrolysis (approximately ±3 percent).

References

Kaufmann, S., and Libby, W. F., 1954, The natural distribution of tritium, Physical Review, v. 93, p. 1337–1344.

Östlund, H. G., and Werner, O. E., 1962, The electrolytic enrichment of tritium and deuterium for natural tritium measurements, *in* Tritium in the physical and biological sciences, Symposium Proceedings (STI/PUB/39) IAEA, Vienna, p. 95–104.

Schroder, L. J., 1971, Determination of tritium in water by the U.S. Geological Survey, Denver, Colo.: U.S. Geol. Survey Rept. USGS–474–134, 22 p.; Avail. *only* from U.S. Dept. Commerce, Natl. Tech. Inf. Service, Springfield, VA 22151.

Tritium
Electrolytic enrichment—liquid scintillation method, Reston lab (R–1174–76)

Parameters and codes: Tritium, dissolved (pCi/l): 07005
Tritium, in water molecules (Tu): 07012

1. Application

The limit of detection of tritium by the liquid scintillation counting method (R–1173–76) is about 60 Tu (190 pCi/l). Many surface-water and most ground-water samples contain less than 60 Tu, and cannot be analyzed directly. Concentration of the tritium in low-tritium samples by electrolysis before counting by liquid scintillation permits the analysis of waters containing as little as 1 Tu (3 pCi/l).

2. Summary of method

When water is decomposed to H_2 and O_2 gas by electrolysis there is a strong isotope fractionation effect which results in the heavier isotopes (tritium in particular) being concentrated in the remaining liquid phase. Under the proper conditions, recovery of more than 70 percent of the initial tritium is possible. Thus, if a sample is reduced from 500 ml to 5 ml by electrolysis, the tritium in the residual 5 ml will have been concentrated by at least: $\frac{500 \times 0.7}{5} = 70$ times. When such an electrolyzed sample is counted using the procedure described in method R–1173–76, tritium levels as low as 1 Tu can be detected.

The electrolysis procedure used is essentially that described by Östlund and Werner (1962). The sample, after distillation, is made basic with NaOH or Na_2O_2 and electrolyzed in glass cells (Östlund cells) with nickel and soft iron electrodes. (See fig. 8, method R–1172–76, for diagram of electrolysis cell.) During operation, the cells are kept at 0°–1°C to improve electrolytic tritium recovery and to minimize loss of sample by evaporation. A maximum of 100 ml is electrolyzed in the cell. If larger samples are to be electrolyzed, the sample is periodically added to the cell from the reservoir as electrolysis proceeds.

Electrolysis proceeds at 6 amperes until less than 25 ml remains. Then the current is reduced in steps to as low as one-half ampere as the remaining volume decreases to the desired 5-ml final volume. Electrolysis from a starting volume of 100 ml requires about 4 d.

Following electrolysis, the sample water is separated from the electrolyte by vacuum distillation and is then ready to be counted.

Electrolysis is performed in sets of cells connected in series to a constant voltage, current-limiting power supply. Each set includes an electrolysis standard, a blank, and from 4 to 10 samples.

3. Interferences

Samples are distilled before and after electrolysis, and are thoroughly gas-stripped by the H_2 and O_2 produced during the electrolysis itself. Thus all potential interfering substances are effectively removed, and no radioactive or other interferences remain in the sample ready for counting.

The major interference with low-level tritium analysis is contamination by tritium [illegible]

self. The electrolyte may contain tritium, or the sample may pick up tritium during excessive exposure to the laboratory atmosphere. To minimize contamination, it is important that sources of tritium above levels naturally present in the air be rigorously excluded from the laboratory. These sources include luminous watches and such high-tritium samples as may result from tracer tests.

Samples of "dead" water should be run through the entire electrolysis and counting process as blanks to monitor contamination and to permit corrections to be made to the final reported tritium content (see section below).

4. Apparatus

The apparatus required is the same as that described in method R–1173–76 with the addition of the following:

Östlund electrolysis cells. (See fig. 8, method R–1172–76.)

Vacuum-distillation apparatus, (1) for predistillation, capable of handling volumes up to 500 ml, and (2) for distillation after electrolysis, capable of handling from 3 to 10 ml.

Freezer for cooling electrolysis cells.

5. Reagents

As specified in method R–1173–76 with the addition of the following:

Electrolyte, NaOH or Na_2O_2.

Electrolysis standard, a tritium standard solution prepared as described in method R–1173–76, sec. 5.2, and containing about 1 dpm/ml.

6. Procedure

Perform electrolytic enrichment as described in sec. 2 above, then follow procedure described in method R–1173–76.

7. Calculations

7.1 Enrichment factor. The enrichment factor, f, required to calculate the sample tritium content from the count data (see method R–1173–76) is calculated using equation 1:

$$f=\frac{V_0}{V_f}\times\frac{V_0^{-(1/\beta)}}{V_f}, \qquad (1)$$

where

V_0 = volume of sample before electrolysis,
V_f = volume of sample following electrolysis, and
β = the separation factor.

The electrolysis standard with each set is counted as if it were a sample and its tritium content determined. Then:

$$f_{std}=\frac{Tu_f}{Tu_0}$$

where

Tu_f = Tritium content of electrolysis standard after electrolysis,
Tu_0 = Tritium content of electrolysis standard before electrolysis, and
f_{std} = standard enrichment factor.

The standard enrichment factor is then substituted for "f" in equation 1 and β is calculated for the set.

7.2 Calculation of tritium concentration. Calculate tritium concentration in the sample in the manner described in method R–1173–76.

8. Report

Report as described in method R–1173–76.

9. Precision

There are uncertainties in each of the terms in equation 1 leading to f. These are the weighing errors in V_0 and V_f, and variations in the electrolysis process itself giving rise to variations in β. Experience suggests that the one standard deviation error of f (σ_f/f in equation 5, method R–1173–76) is about 5 percent.

There is also error associated with the value of the blank which is used to correct for sample contamination by reagents and exposure in the laboratory. Under favorable conditions, the error in the blank may be as

small as ±0.02 Tu (Östlund and others, 1974). In routine work, the error in the blank is taken as equal to the value of the blank correction itself—usually from 0.1 to 0.3 Tu. Thus, although it is sometimes possible to count a sample to a precision of better than 0.1 Tu, the real precision of routine tritium analyses is limited by the blank error to ±0.1 to ±0.3 Tu.

References

Östlund, H. G., and Werner, E., 1962, The electrolytic enrichment of tritium and deuterium for natural tritium measurements: *in* Tritium in the Physical and Biological Sciences; Internat. Atomic Energy Agency, Vienna, V.I., p. 95–104.

Östlund, H. G., Dorsey, H. G., and Rooth, C. G., 1974, Geosecs North Atlantic radiocarbon and tritium results: Earth and Planet. Science Letters, v. 23, p. 69–86.

Uranium, dissolved
Fluorometric method—direct (R-1180-76)

Parameters and codes: Uranium, dissolved (μg/l): 22703
Uranium, dissolved (pCi/l): 80010

1. Application

The method is suitable for the determination of uranium in nonsaline waters (<10,000 mg/l dissolved solids) in which uranium fluorescence is quenched less than 30 percent. If quenching exceeds 30 percent, it is advisable to use the extraction method. The latter method is much more time consuming. Therefore, it is usual practice to apply the direct fluorimetric method as a first step unless previous analysis of samples from a particular area has shown that the simple approach is not possible.

The minimum detection limit varies with the properties of the sample, flux, and fluorimeter, but is normally 0.3 μg/l.

2. Summary of method

The fluorimetric method of determining uranium is among the most sensitive and specific of analytical methods. The intense fluorescence of uranium when fused in a sodium fluoride-sodium carbonate-potassium carbonate flux is utilized to determine quantitatively the amount of uranium present in the sample. In its simplest form the analysis is carried out by fusing a dry residue of the evaporated-water sample in fluoride-carbonate flux, allowing this to solidify into a small disk, and determining the fluorescence under ultraviolet light in a reflection-type fluorimeter. Chromium, copper, manganese, and a few other elements in water quench the fluorescence in varying degree. When the quenching elements are in relatively low concentration, quench-compensation techniques may be used. When quenching elements are present in relatively high concentration, it is necessary to purify the uranium by extraction. This technique is described as "Fluorometric method—extraction procedure" (R-1181-76).

Although the fluorescence of the sample is directly proportional to the uranium concentration (disregarding quenching effects), it is not possible to use a constant calibration straight-line plot of fluorescence against concentration. This is a result of variation in properties between batches of flux, variations in the fluxing temperature, possible surface oxidation during fluxing, and variations of uranium impurity in different batches of flux. The above effects are minimized by running uranium standards with each set of samples so that a new calibration of concentration against fluorescence is made under the conditions existing for each set of analyses.

The materials used for the preparation of the flux always contain a small amount of uranium. Fluorescence from this source plus reflected light not absorbed by the filters in the fluorimeters make up the blank. The fluorescence component of the blank is subject to quenching while the reflectance component is not. The blank for a highly quenched sample is, therefore, less than the blank for a sample with relatively low quenching. A graphical method of compensating for this effect on the blank value was developed by Thatcher and Barker (1957).

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The following method is similar to that described in Water-Supply Paper 1696–C (Barker and others, 1965) for the determination of uranium in nonsaline water.

3. Interferences

Direct spectral interference is not a problem in the fluorimetric method. Cadmium fluoresces in high carbonate flux disks at approximately the same wavelength as uranium (Booman and Rein, 1962, p. 102), but interference from this source is unlikely in most natural waters. High concentrations of salt cause difficulty in the preparation of the flux disks. The quenching effect of transition metals has been cited above.

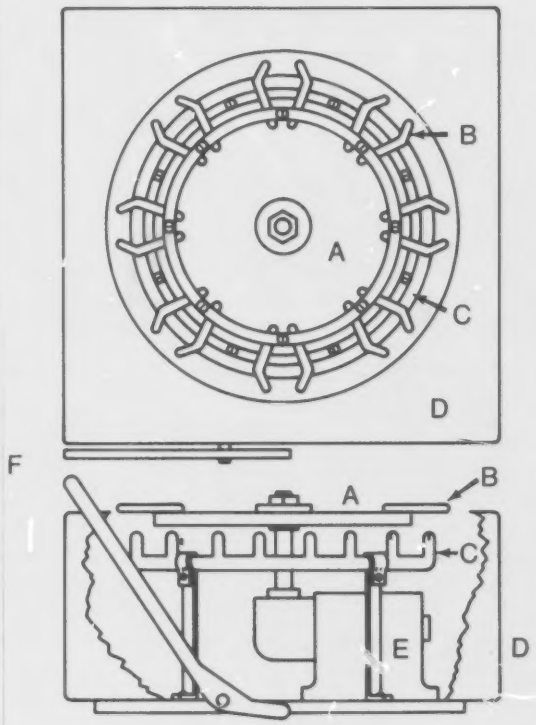
4. Apparatus

4.1 *Crucible tongs*, platinum tipped for holding hot platinum dishes.

4.2 *Fluorimeter*. A reflection-type instrument of high sensitivity equipped with a sample carriage to accept small disk-shaped solid samples is required. The sample cavity should be approximately 35 mm in diameter and 5-mm deep. Instructions herein pertain to the Jarrell-Ash Model 26–000 instrument, but any fluorimeter that fulfills the above requirements may be used.

4.3 *Fusion apparatus*. The rotary fusion machine developed by Stevens and others (1959) and modified by Barker and others (1965) is used (fig. 9). A rotating sample carriage is mounted above a ring of burners and is slowly revolved during the fusion to assure that each sample receives the same heating. The samples are contained in platinum fusion dishes resting on quartz rods. The fusion unit is tilted approximately 30° during part of the fusion so that molten flux washes the sides of the fusion dishes to sweep down any sample residue that may adhere. The design of the burner must be adapted to local gas composition and pressure to obtain the optimum temperature.

4.4 *Fusion dishes*. The dishes are fabricated of platinum to a shallow-dish shape that provides maximum exposure of sample disk surface (for high fluorescence sensitivity) compatible with adequate thickness for strength (fig. 10). The rounding of the bottom permits easy removal of the solidified



A - ROTATING SAMPLE TABLE

B - QUARTZ RODS TO HOLD PLATINUM DISHES

C - RING BURNER

D - SHEET METAL HOUSING

E - GEARED MOTOR

F - LEVER FOR INCLINING BURNER 20°

Figure 9.—Stevens apparatus for fusion and mixing of sample and flux in uranium determination.

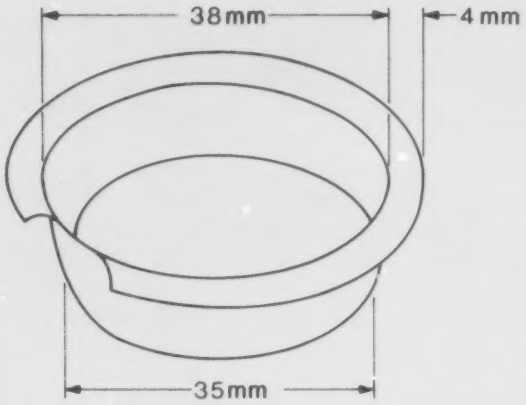


Figure 10.—Platinum dish for use in Stevens apparatus.

flux disk. An identifying number is stamped into the lip of each dish.

4.5 *Infrared drying lamps:* Dual 250-watt infrared drying lamps in a protective metal shield are mounted on a ringstand for variable heat adjustment.

4.6 *Micropipet,* 50-μl capacity, Eppendorf type, for addition of uranium standard.

4.7 *Mill.* A 5- to 6-liter Pyrex glass-jar mill containing 15 cm by 2.5 cm cylindrical Lucite rods is used to mix the flux.

4.8 *Pipets,* volumetric 1-, 2-, 3-, 4-, 5-, 6- and 10-ml.

4.9 *Polyethylene jars,* wide-mouth, 4-liter screw-capped, for storing flux.

5. Reagents

5.1 *Chromium solution,* 1 ml = 30 μg Cr: Dissolve 0.085 g of $K_2Cr_2O_7$ in distilled water and dilute to 1,000 ml. Weight and volume measurements need not be exact.

5.2 *Copper solution,* 1 ml = 60 μg Cu: Dissolve 0.236 g of $CuSo_4 \cdot 5H_2O$ in distilled water and dilute to 1,000 ml. Weight and volume measurements need not be exact.

5.3 *Manganese solution,* 1 ml = 20 μg Mn: Dissolve 0.081 g of $MnSo_4 \cdot 5H_2O$ in distilled water and dilute to 1,000 ml. Weight and volume measurements need not be exact.

5.4 *Sodium fluoride solution,* 1 ml = 0.01 g NaF: Dissolve 10 g of dry sodium fluoride in distilled water and dilute to 1,000 ml.

5.5 *Uranium standard solution* I, 1 ml = 100 μg U: Dissolve 0.1773 g of reagent-grade uranyl acetate dihydrate in approximately 500 ml of distilled water. Add 10 ml of concentrated nitric acid and dilute to 1,000 ml in a volumetric flask. Store in a Teflon bottle.

5.6 *Uranium standard solution* II, 1 ml = 1.00 μg U: Dilute 10.0 ml of uranium standard solution I to 1,000 ml with distilled water. Store in a Teflon bottle.

5.7 *Flux:* Using anhydrous powdered reagent-grade chemicals, weigh out 910 g of Na_2CO_3, 910 g of K_2CO_3, and 180 g of NaF, and rough-mix in the glass-jar mill using a large porcelain spatula, or Lucite rod. Add the small Lucite rods, stopper tightly with a polyethylene stopper, place the jar on the mechanical rollers, and dry-mix overnight.

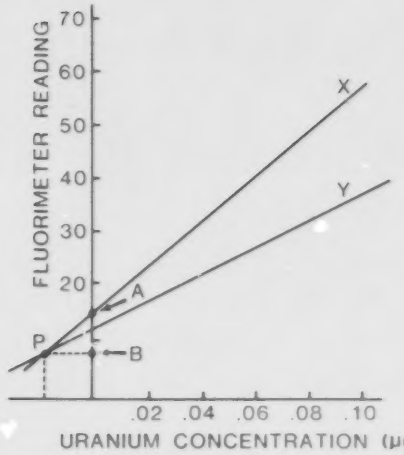
6. Procedure

6.1 Determination of flux constants: It is necesary to determine r (the fraction of reflected light in the blank) and f (the fraction of fluorescent light in the blank) for each batch of flux. These "flux constants" are used for all analyses made with the given batch of flux. Two calibration curves are prepared as shown in figure 11. The calibration curve X is prepared with pure uranium solutions and the calibration curve Y is prepared with uranium solutions containing a constant amount of quenching agent. The two curves intersect (P) at a negative uranium concentration. The intersection of the curve X with the fluorescence axis is point A, the unquenched blank. The intersection P of X and Y is point B, the reflected light. The fraction of reflected light r is B/A and the fraction of fluorescent light f in the blank reading is $1-r$.

The procedure is as follows:

6.1.1 Measure 1 ml of sodium fluoride solution and the following volumes of uranium standard solution II (microburet) into platinum fusion dishes.

Dishes	Solution II (ml)
1 and 2	0.000
3 and 4	.020
5 and 6	.040
7 and 8	.060
9 and 10	.080



X-FLUORESCENCE (UNQUENCHED)
Y-FLUORESCENCE (QUENCHED)
A-FLUORESCENCE BLANK (UNQUENCHED PLUS REFLECTED LIGHT)
B-REFLECTED LIGHT
P-INTERSECTION POINT

Figure 11.—Uranium calibration curve.

6.1.2 To the even-numbered dishes, add 1 ml of chromium solution.

6.1.3 Evaporate the solutions to dryness under the infrared lamps. Do not permit the samples to bake as this can result in loss of uranium, although the sodium fluoride added as the first step minimizes loss by overheating.

6.1.4 Fusion procedure: To each of the dishes add 2 g of the flux mixture. Spread and bank the flux with a glass rod so that any solids on the vertical walls of the dishes will be covered.

6.1.5 Place the dishes on the rotating table of the Stevens fusion apparatus, and incline it by operating the positioning lever. Ignite the burner ring, adjust to maximum heat, and heat the dishes until the flux is completely melted. This requires about 5 min. Allow the fusion table to rotate in the inclined position for an additional 2 min. Return the table to the level position, and continue heating the melt for an additional 3 min at the same temperature.

6.1.6 Turn the heat control to the intermediate setting and heat at this temperature for 3 min.

6.1.7 Turn to the low setting and heat for 3 min. Turn off the burner and allow the dishes to cool for 8 min with the fusion table still rotating. Finally, place the dishes in a desiccator, and cool for at least 30 min before measuring fluorescence.

6.1.8 Measurement of fluorescence: The following instructions apply to the Jarrel-Ash fluorimeter. Modify if other fluorimeters are used. Allow the instrument to warm up 30 min before use.

6.1.9 Set the fluorimeter reading to zero using the zero-adjustment knob. Push the empty sample tray all the way in, depress the X.01 key, and adjust to zero using the screw adjustment. Remove the blank flux disk from the platinum dish by inverting it on a clean piece of paper. Place the disk in the fluorimeter tray and push into measurement position. Depress the X.1 key and adjust the sensitivity so that a reading of 10 (on a scale of 100) is obtained for the blank.

6.1.10 Remove the blank disk and recheck the zero setting. Use a soft-bristle brush to remove any particles sloughed into the sample tray from the preceding disk. If the zero needs readjustment, repeat step 6.1.9 until the empty holder reading is zero when the blank reading is 10. The "fluorescence" reading of the empty holder is minimized by painting with a colloidal graphite mixture such as Aqua-dag. This must dry before use. Repainting is required at intervals.

6.1.11 Read the fluorescence of the standard and sample disks using the X.1 scale, if possible, or X1 and X10 scales if needed.

6.1.12 Plot the fluorescence of the disks as a function of the weight of uranium (fig. 11). Draw the best straight lines X and Y through the sets of points for the quenched and unquenched disks. Determine B, A, and r and f as above.

6.1.13 Repeat the calibration substituting 1 ml of manganese solution for the chromium solution.

6.1.14 Repeat the calibration substituting 1 ml of copper solution for the chromium solution.

6.1.15 Average the values of r and f determined for the three quenching elements as above. These mean values of r and f are used for all analyses using this batch of flux.

6.2 Analysis of the water sample.

6.2.1 Four samples may be analyzed simultaneously using the Stevens fusion apparatus with 20 positions for samples, when analyses are run in duplicate. One milliliter of sodium fluoride solution is added to the 20 platinum dishes. Two dishes serve as blanks. Standard uranium (0.06 μg) is added to each of two dishes. Four 7-ml aliquots of each sample are pipetted into four dishes. Standard uranium (0.06 μg) is added to two of them.

6.2.2 Proceed with the analysis as in steps 6.1.3 through 6.1.11 above.

7. Calculations

7.1 Determine the quenching factor, Q, for each sample from the equation:

$$Q = \frac{D-A}{C-B} = \frac{\Delta I_s}{\Delta I_n},$$

where

Q = ratio of uranium fluorescence under quenching conditions to the fluorescence under no quench, for a given sample,

A = mean fluorimeter reading of unspiked samples,

B = mean fluorimeter reading of blank disks,

C = mean fluorimeter reading of standard disks,

D = mean fluorimeter reading of sample disks containing uranium spike,

ΔI_s = fluorescence increment of spiked sample, and

ΔI_n = fluorescence of the standard.

Note that the equation applies only when the amount of uranium spike in the sample is equal to uranium in the standard.

7.2 Calculation of the corrected blank value for each sample: The blank value to be used with an individual water sample must be somewhat less than the blank measured instrumentally on the pure sodium fluoride-sodium carbonate disk because of quenching in the water sample of that portion of the blank value contributed by uranium impurity in the flux. Since a blank that represents conditions in the sample cannot be prepared, it is necessary to calculate the blank value for each sample on the basis of the blank measured for the disk of pure fluoride-carbonate flux. The contribution of reflected light to the blank is assumed to be the same for the sample disks and the pure flux disk. The calculation is simply:

$$B_s = (QfB_f) + (rB_f),$$

where

B_s = sample blank.

B_f = blank obtained with disk of pure flux,

f = fraction of fluorescent light for the batch of flux used,

r = fraction of reflected light for the batch of flux used, and

Q is defined in section 7.1.

7.3 Concentration of uranium in the sample: This is calculated using equation:

$$\text{g/l of U} = \frac{S}{\Delta I_n}\left[\frac{A-B_s}{Q}\right]\left[\frac{1{,}000}{V}\right],$$

where

S = micrograms of uranium in the standard, and

V = sample volume in ml and the other terms are as defined in sections 7.1 and 7.2.

If it is known from previous experience with water from a particular source that the quenching factor Q is always greater than 0.7 (quenching less than 30 percent), it becomes possible to omit the determination of Q and combine equations under 7.1 and 7.3 to obtain the following simplified expression:

$$\mu\text{g/l of U} = \frac{S(A-B_s)}{\Delta I_s}\left[\frac{1{,}000}{V}\right].$$

8. Report

Report concentrations less than 1.0 μg/l to one significant figure. Above 1.0 μg/l, report two significant figures. Occasionally the radioactivity is reported in pCi/l. The conversion factor is 1 μg = 0.33 pCi when only the radioactivity of uranium-238 is considered. Natural uranium contains 0.72 percent of uranium-235, and normally uranium-238 is considered to be in equilibrium with an equal activity of uranium-234. The conversion factor is 1 μg = 0.68 pCi when all three isotopes are included.

9. Precision

Precision is approximately ±MDL or ±15 percent, whichever is larger. The MDL is a function of quenching, fluorescence intensity of the flux, and uranium impurity in the flux. It may be as low as 0.1 μg/l with a sample having no significant quenching analyzed with a relatively pure flux, and as high as 0.5 μg/l when a highly quenched sample is analyzed with a flux having relatively high uranium impurity. Under average conditions the MDL is 0.3 μg/l.

References

Barker, F. B., Johnson, J. O., Edwards, K. W., and Robinson, B. P., 1965, Determination of uranium in natural waters: U.S. Geol. Survey Water-Supply Paper 1696–C, 25 p.

Booman, G. L., and Rein, J. E., 1962, Uranium *in* Kolthoff, I. M., and Elving, P. J., eds., Treatise on analytical chemistry, pt. 2 *of* Analytical chemistry of the elements, sec. A. Systematic analytical chemistry of the elements: New York, Intersci. Publishers, v. 9, p. 1–188.

Stevens, R. E., Wood, W. H., Goetz, K. G., and Horr, C. A., 1959, Machine for preparing phosphors for the fluorimetric determination of uranium: Anal. Chemistry, v. 31, p. 962–964.

Thatcher, L. L., and Barker, F. B., 1957, Determination of uranium in natural waters: Anal. Chemistry, v. 29, p. 1575–1578.

Uranium, dissolved
Fluorometric method—extraction procedure (R–1181–76)

Parameters and codes: Uranium, dissolved (μg/l): 80020
Uranium, dissolved (pCi/l): 80015

1. Application

The method is applied to water samples where the reduction of uranium fluorescence by quenching exceeds 30 percent (as determined in "Fluorometric method—direct" (R–1180–76)), the concentration of total dissolved solids exceeds approximately 10,000 mg/l, or a minimum detection level lower than 0.3 μg/l is desired.

2. Summary of method

Uranium is separated from quenching elements and excessive salt concentrations in a two-step separation procedure developed by Smith and Grimaldi (1954). Uranium is coprecipitated, as uranyl phosphate, on aluminum phosphate from a large-volume water sample. Several quenching elements are carried down by the precipitate. Final purification is made by dissolving the phosphate precipitate in dilute nitric acid and extracting with ethyl acetate or ethyl ether in the presence of a salting agent. The organic solution is evaporated to dryness in a platinum dish, and the fluorescence is determined after fusion of the dry residue in sodium fluoride-sodium carbonate flux.

Barker and others (1965) modified the procedure slightly and evaluated the application to natural waters. The present procedure uses magnesium nitrate (Hellman and Wolf, 1952) to "salt-out" uranium from the nitric acid solution of the precipitate into the ethyl ether phase. The magnesium salt is slightly more effective than the aluminum salt and usually contains less uranium impurity, thus giving a lower blank correction.

3. Interferences

All interferences in natural waters are removed by the separation steps and have no effect. The method has not, however, been extensively tested with industrial wastes, mine waters, and other waters that may have unusually high concentrations of heavy metals. When such waters are encountered it is advisable to run a spiked sample containing a known increment of uranium through the analytical procedure to test for possible residual quenching. A quenching correction can then be made as in "Fluorometric method—direct" (R–1180–76) based on the percentage of reduction of the expected fluorescence from the known increment of uranium.

4. Apparatus

4.1 *Centrifuge.*

4.2 *Centrifuge tubes,* 40- or 50-ml capacity Pyrex tubes with polyethylene screw-type caps.

4.3 *Evaporating dishes,* Teflon, 125 ml.

4.4 *Fluorimeter:* See method R–1180–76.

4.5 *Fusion apparatus:* See method R–1180–76.

4.6 *Fusion dishes:* See method R–1180–76.

4.7 *Micropipet,* 50-μl-dispensing pipet, Eppendorf type.

4.8 *Pipet and control,* 5 ml.

4.9 *Polyethylene jars:* See method R–1180–76.

4.10 *Ultrasonic generator,* 500-watt model.

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5. Reagents

5.1 *Aluminum nitrate solution*, 0.2 *M*: Dissolve 15 g $Al(NO_3)_3 \cdot 9H_2O$ in distilled water and dilute to 200 ml.

5.2 *Ammonium hydroxide*, concentrated.

5.3 *Ammonium nitrate solution*, 1 ml = 10 mg NH_4NO_3: Dissolve 10 g of reagent-grade ammonium nitrate in distilled water and dilute to 1,000 ml.

5.4 *Diammonium hydrogen phosphate solution*, 0.090 *M*: Dissolve 12 g of $(NH_4)_2HPO_4$ in distilled water and dilute to 1,000 ml.

5.5 *Ethyl ether.*

5.6 *Magnesium nitrate reagent*, 5.0 *N* in $Mg(NO_3)_2$, 0.5 *N* in HNO_3: Dissolve 640 g of $Mg(NO_3)_2 \cdot 6H_2O$ in the minimum volume of hot distilled water in a 1-litre beaker. Pour into a 1,000-ml volumetric flask, add 32 ml of concentrated HNO_3, dilute to volume, cool to room temperature, and again dilute to volume.

5.7 *Methyl red indicator solution:* Dissolve 0.1 g of methyl red (dimethylaminoazobenze-necarboxylic acid) in 250 ml of 60 percent ethanol.

5.8 *Nitric acid*, concentrated.

5.9 *Uranium standard solution* I, 1 ml = 100 μg U: See method R–1180–76.

5.10 *Uranium standard solution* II, 1 ml = 1.0 μg U: See method R–1180–76.

5.11 *Uranium standard solution* III, 1 ml = 0.01 μg U: Pipet 10 ml of uranium standard solution II and 5 ml of concentrated HNO_3 into a 1,000 ml volumetric flask, and dilute to volume with distilled water. Mix thoroughly, and store in a Teflon bottle.

6. Procedure

6.1 Place 400-ml aliquots of the filtered samples in 600-ml beakers. Prepare two standards by addition of 8.0 ml of uranium standard solution III to 400 ml of distilled water in 600-ml beakers. Also prepare a blank of 400 ml of distilled water. An additional blank and standard (prepared by pipetting 50 μl of uranium standard solution II directly into the platinum dish) are taken through steps 6.11 through 6.19 of this procedure.

6.2 Add 3 ml of concentrated HNO_3, 1 ml of 0.2 *M* aluminum nitrate reagent, and 5 ml of 0.090 *M* diammonium-hydrogen phosphate reagent. Heat to boiling to remove carbon dioxide.

6.3 Add a few drops of methyl red indicator, and neutralize just to the yellow endpoint by dropwise additions of concentrated ammonium hydroxide with constant stirring. If, on addition of the indicator, a pink color forms and then disappears, the water probably contains an excessive amount of iodide or bromide ions. In that event, add ammonium hydroxide, 2 or 3 drops at a time; then add a drop of indicator. Repeat this procedure until the indicator exhibits the yellow color instantly upon hitting the solution.

6.4 Digest the precipitate near the boiling point on a hotplate or steam bath for 30 min; then allow to cool to room temperature and settle.

6.5 Using a small pipet connected to an aspirator, draw off as much of the supernate as possible without disturbing the precipitate.

6.6 Transfer the precipitate to a 40- or 50-ml screw-cap Pyrex centrifuge tube. Police the beaker and the stirring rod with 1 percent ammonium nitrate solution, adding the washings to the centrifuge tube. Centrifuge, discard the supernate, and add 4 or 5 ml of the 1-percent ammonium nitrate solution. Agitate the mixture in the tube to wash the precipitate, and again centrifuge and discard the supernate. Note: In transferring the precipitate to the centrifuge tube it will probably be necessary to centrifuge and decant once before the transfer can be completed.

6.7 Ovendry the precipitate in the centrifuge tube for 15–20 minutes at 80°C. Raise oven temperature to approximately 100°C and take to complete dryness.

6.8 Add 8 ml of the $Mg(NO_3)_2$ reagent, and warm gently to dissolve the precipitate. Use the ultrasonic generator to speed dissolution.

6.9 When cool, add 10 ml of cold ethyl ether to the test tube, cap, and agitate vigor-

ously for at least 2 min. Allow about 15 min for the two layers to separate.

6.10 Pipet off 5.0 ml of the ethyl ether layer using a 5-ml pipet with a control, and place in a 125-ml Teflon dish to which approximately 8 drops of water have been added. Add another 5 ml of ether to the tube, cap, and agitate for 2 min. Again, allow 15 min for the layers to separate, then pipet an additional 5 ml of the ethyl ether layer from the tube into the same Teflon dish. Use the ultrasonic generator to break up emulsions. The equivalent volume transferred is thus 7.5 ml of the original 10 ml of ether added.

6.11 Allow the ethyl ether to evaporate completely in a fume hood at room temperature. Heat gently on a hotplate to complete dryness.

6.12 Transfer the sample from the Teflon evaporating dish to the platinum dish used for fusion with a small portion of ethyl alcohol, policing the bottom and the sides of the Teflon dish thoroughly with a small rubber policeman. Repeat the ethyl alcohol wash one more time. A third wash must be completed using a small portion of distilled water. Combine with the ethyl alcohol washes immediately. The three washes must be kept small enough so the combined washes do not exceed the volume of the platinum fusion dish. (Here again the distilled water wash serves a double purpose: (1) assures complete transfer of the sample, and (2) reduces the ethyl alcohol creep up the sides of the fusion dish.) Take fusion dish to dryness under a heat lamp.

6.13 Carefully flame fusion dish over a burner until the dish is a dull red.

6.14 Add 2 g of flux and prepare fluorescent disk as in method R–1180–76.

6.15 Place the dishes in a desiccator, and cool for at least 30 min. Determine the fluorescence of the samples, blank, and standard as in method R–1180–76.

7. Calculations

Concentration of uranium is calculated from the equation:

$$\mu g/l \text{ of } U = \frac{1{,}000\,S(A-B)}{V(C-B)}\,\frac{R_n}{R_s},$$

where

S = μg of uranium added to prepare the standards,
A = mean fluorimeter reading of the sample disks,
B = mean fluorimeter reading of the blank disks,
C = mean fluorimeter reading of the standard disks,
V = volume of the sample in milliliters,
R_s = fractional recovery of uranium extracted from the sample, and
R_n = fractional recovery of uranium extracted from the standard.

The fraction of uranium recovered in serial extraction of the samples and standards (R_s, R_n) is determined by equation:

$$R = \frac{v_1}{V_1} + 1\left(\frac{v_1}{V_1}\right)\left(\frac{v_2}{V_2}\right) + 1\left[-\frac{v_1}{V_1} - \left(1-\frac{v_1}{V_1}\right)\left(\frac{v_2}{V_2}\right)\left(\frac{v_3}{V_3}\right) + \cdots\left[\ \right]\left(\frac{v_4}{V_4}\right)\right.,$$

where

v = volume of ether (ml) removed after each extraction, and
V = volume of ether (ml) in the sample for each extraction.

When V is equal to 10 ml and v is equal to 5 ml (normal procedure) the R values for the first, second, third, and fourth extractions are respectively 0.5, 0.75, 0.875, and 0.937.

When the serial extraction of the sample is identical to the serial extraction of the standard (same number of extractions using the same volumes) the fractional recoveries cancel and the equation simplifies to:

$$\mu g/l \text{ of } U = \frac{1{,}000\,S(A-B)}{V(C-B)}.$$

8. Report

Report concentrations to two significant figures above 0.10 $\mu g/l$ and to one significant figure for values below 0.10 $\mu g/l$ with 0.01 $\mu g/l$ as the minimum.

9. Precision

Minimum detectable concentration is 0.01 μg/l. The precision of the fluorescence methods for determination of uranium is governed primarily by conditions in the flux and in the fusion operation. Reproducibility of the fluorescence from replicates standards averages ±15 percent. The same value is used for precision of sample runs except at concentrations below approximately 0.07 μg/l where ±MDL represents the precision.

References

Barker, F. B., Johnson, J. O., Edwards, K. W., and Robinson, B. P., 1965, Determination of uranium in natural waters: U.S. Geol. Survey Water-Supply Paper 1696–C, 25 p.

Hellman, N. N., and Wolfe, M. J., 1952, Influence of various nitrates on the diethyl ether extraction of low concentrations of uranium from thorium, *in* Production and Separation of Uranium-233 (ed., L. Katzin): U.S. Atomic Energy Comm. TID 5223, pt. 1.

Smith, A. P., and Grimaldi, F. S., 1954, The fluorimetric determination of uranium in nonsaline and saline waters, *in* Collected papers on methods of analysis for uranium and thorium: U.S. Geol. Survey Bull. 1006, p. 125–131.

Uranium, dissolved, isotopic ratios
Alpha spectrometry—chemical separation (R–1182–76)

Parameter and code: Uranium, dissolved, isotope ratio (dimensionless): none assigned

1. Application

The method is applicable to most freshwater and saline waters. Industrial wastes and mine drainage may require special treatment.

2. Summary of method

The uranium isotopes are determined by alpha spectrometry after concentration and separation from the bulk of the water sample by use of the precipitation-extraction procedure described under method R–1181–76 determination of uranium. This is followed by an ion-exchange procedure to eliminate thorium, an alpha-emitting radionuclide. The final step is electrodeposition of the uranium (as uranium oxide) in a very thin layer on a metal disk. Electrodeposition conditions are critical because thick or nonuniform deposition must be avoided, and interfering radioisotopes must be kept in the solution phase. Thick or nonuniform electrodepositions result in distortion of the alpha energy peaks and reduced counting efficiency. The procedure is described in detail by Edwards (1968).

Alpha spectroscopy is carried out by means of a silicon surface-barrier detector with output to a linear amplifier and multichannel analyzed. Readout is by means of an x–y plotter and electric typewriter which prints out counts in each energy channel.

The alpha spectra of the uranium isotopes are as follows:

Uranium-238; 4.195 MeV (0.77), 4.147 MeV (0.23)
Uranium-235; 4.370 MeV (0.25, 4.354 MeV (0.35), (with five other energy peaks of less intensity)
Uranium-234; 4.768 MeV (0.72), 4.717 MeV (0.28).

Since surface-barrier detectors can be obtained with resolution as fine as 0.030 MeV (30 keV) (for 450 mm² counting area), it is possible to cleanly resolve all the uranium peaks of interest.

Because of the very low radioactivity of uranium, it may be necessary to collect the uranium from a relatively large water sample to yield between 2.5 and 220 μg of uranium. Samples as large as 25 liters can be used.

3. Interferences

There is no direct spectral overlap by other natural alpha-emitting nuclides. However, if thorium-230 or protoactinium-231 are present in great excess, broadening of their peaks might introduce a small error. Transition metals, when present in great excess, might be carried through the final electrodeposition to increase the mass of the deposit. This would broaden the alpha energy peaks and reduce the counting efficiency. None of these possible adverse effects have yet been encountered in practice.

4. Apparatus

4.1 *Detector*, silicon surface-barrier detector with approximately 450 mm² sensitive area and depletion depth of 60 microns or more.

4.2 *Vacuum chamber*. The detector is mounted in a chamber which is evacuated

after the sample is inserted. This is essential to minimize scattering of alphas by air. A vacuum pump and silica-gel moisture trap are used to maintain vacuum at 0.1 torr.

4.3 *Multichannel analyzer array.* The signal is fed from the detector through a preamplifier and linear amplifier into a multichannel analyzer where the alpha energy pulses are routed to their appropriate channels in the memory. The analyzer should have a minimum of 256 channels if the full resolution capability of the best silicon barrier detectors is to be realized.

4.4 *Readout system.* The memory may be read out using a plotter, teletype unit, punched tape, magnetic tape, or other appropriate means. The combination of x–y plotter and electric typewriter has been found to be satisfactory.

4.5 *Chemical-separation apparatus.* The chemical apparatus required for method R–1181–76 (items 4.6 to 4.8) are used.

4.6 *Ion-exchange columns.* These are designed to hold 40 ml of liquid in a funnel top and to pass the solution through a 14-cm length of ion-exchange resin, 1 cm in diameter.

4.7 *Electrolysis apparatus.* The cell is designed to plate a circular deposit 2.2 cm in diameter to correspond with the sensitive diameter of the alpha detector. The deposit is collected on a titanium disk which is clamped onto the bottom of a Teflon cylinder thus forming an electrolysis cup. The titanium disk is the cathode. The anode is a flat coil of platinum wire suspended 2.2 cm above the titanium disk. Power is supplied by a small 12-volt rectifier with voltmeter and ammeter. The titanium disks are 3.2 cm in diameter.

5. Reagents

5.1 *Electroplating reagents,* NH_4Cl solution, 2 *N;* acetone; and ammonia.

5.2 *Ion-exchange reagents,* Bio-Rad AG 1–X8, 50–100 mesh or equivalent. Hydrochloric acid, 8 *N* and 0.1 *N*.

5.3 *Precipitation-extraction reagents.* All reagents required for the precipitation-extraction steps of method R–1181–76 are used.

6. Procedure

6.1 Determine the volume of sample required by carrying out the fluorimetric uranium analysis by method R–1180–76 or R–1181–76 as indicated by the nature of the sample. The maximum weight of uranium that can be used in the isotopic analysis is 220 μg and the minimum is 2.5 μg. Recommended sample volumes for a thousandfold range of uranium concentrations are given in table 2.

Table 2.—Recommended sample volumes, minimum, and reduced volumes for isotopic uranium analysis

U concentration (μg/l)	Volume, in liters		
	Recommended	Minimum	Reduced volume
0.10	25	25	5
.2	25	12.5	5
.3	25	8.4	5
.4	20	6.3	4
.5	20	5.0	4
.6	20	4.2	4
.8	20	3.2	4
1.0	20	2.5	4
1.2	20	2.1	4
1.5	20	1.7	4
2.0	15	1.25	3
3.0	10	.84	2
5.0	10	.50	2
7.0	5	.36	1
10	5	.25	1
12	5	.21	1
15	5	.17	1
20	2	.13	1
30	2	.084	1
50	2	.050	1
70	1	.036	1
100	1	.025	1

6.2 If the sample volume exceeds 1 liter, evaporate on a hotplate to the reduced volume value shown in table 2. If the reduced volume exceeds 1 liter it is necessary to divide the sample into two or more 1-liter portions. Each portion is carried through the procedure as an individual sample through step 6.3. Run a blank of 1-liter distilled water through the procedure.

6.3 Carry out the uranium extraction procedure, method R–1181–76, steps 6.2 through 6.11. If two or more 1-liter portions of one sample are extracted, combine the extracts before step 6.11.

6.4 Dissolve the dry residue that remains from the evaporation of the ether layer in 10 ml of 8 *N* HCl.

6.5 Prepare the ion-exchange columns by washing 6 g of resin in a beaker with 8 *N* HCl. Transfer to the columns and wash with 8 *N* HCl.

6.6 Pour the solution from [illegible] into the ion-exchange tube. Allow to flow through at the rate of 20–30 drops per minute. Elute thorium with 50 ml of 8 *N* HCl and discard this eluate. Elute uranium with 60 ml of 0.1 *N* HCl.

6.7 After evaporating to dryness, adding HNO_3, and evaporating again to eliminate the last traces of HCl, prepare the residue for electrolysis by dissolving in the electrolyte, 10 ml of 2 *N* NH_4Cl.

6.8 Transfer to the electrolysis cell, and plate the uranium onto the titanium disk using current of 1 ± 0.1 ampere. Electrolyze for 100 min.

6.9 Introduce the dry sample on the titanium disk into the vacuum chamber, pump down to 0.1 torr, and count the alpha activity of the sample for 1,000 min using the energy range 3.8–5.3 MeV.

6.10 Printout the spectrum with the x–y plotter and the typewriter.

7. Calculations

7.1 Identify the uranium isotopes present on the basis of the x–y plot, using the data from the typed readout, establish the count under the principal alpha energy peak for each isotope by summing the counts and subtracting the blank. Since background for the samples and the blank is the same when normalized to the same counting time, this also corrects for background.

The isotopic ratio is:

$$R = \frac{\text{U-234}}{\text{U-238}} = \frac{C\text{-}234}{C\text{-}238},$$

where

C–234 = counts under the 4.763 MeV peak corrected for blank, and
C–238 = counts under the 4.195 MeV peak corrected for blank.

7.2 Determine concentration of each uranium isotope, if desired, by applying the isotope ratio to the concentration of total uranium as determined by fluorescence method R–1180–76 or R–1181–76.

8. Report

Report activity ratios less than one to two significant figures. Report activity ratios greater than one to three significant figures.

9. Precision

There are insufficient data to establish a reliable experimental standard deviation. Standard deviation based on counting statistics may be calculated using the following:

$$\sigma = R\left(\frac{(C\text{-}234)+B+1}{((C\text{-}234)-B)^2} + \frac{(C\text{-}238)+B+1}{((C\text{-}238)-B)^2}\right)^{1/2},$$

where

B = experimentally determined blank.

Derivation of the equation may be found in Edwards (1968).

Reference

Edwards, K. W., 1968, Isotopic analysis of uranium in natural waters by alpha spectrometry: U.S. Geol. Survey Water-Supply Paper 1696–F, 26 p.